CHEMISTRY LIBRARY
Jun 17 1957

JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY

VOL. XXXIV FEBRUARY, 1957 NO. 2

UNIVERSITY OF MINNESOTA
MAY 27 1957

CONTENTS

PAGE

15. Friedel-Crafts' reaction involving unsaturated ketones and esters. Part VII. Alkylation of *ortho*- and *para*-cresol methyl ethers with ethyl allylacetate and allylacetone.—By O. P. Vig, S. S. Sandhu and S. M. Mukherji ... 81
16. Studies in the chemistry of tellurium. Part I. The behaviour of tellurium on cathodic and anodic polarisation.—By H. Khalifa and I. M. Issa ... 87
17. The reactivity of thiol groups in proteins. Part III. Human, bovine and horse serum-albumins.—By R. Lontie and G. Beckers 93
18. Experiments on the syntheses of furano compounds. Part X. 2-Phenyl-coumarones.—By J. N. Chatterjea and S. K. Roy 98
19. The hydrolytic constant and heat of hydrolysis of hydroxylamine hydrochloride.—By S. S. Muhammad, D. Hanmanth Rao and M. A. Haleem ... 101
20. 2 : 6 - Diaryl-3-ethoxycarbonyl - 4 - piperidones and their derivatives.—By P. N. Bhargava and K. P. Singh 105
21. On some features of the titration curves of carbonic acid and phosphoric acid with baryta.—By R. P. Mitra and Hakam Singh 109
22. Potentiometric determination of tripositive antimony with alkaline hypochlorite.—By (Miss) Sufura Khatun and M. H. Khundkar 114
23. The constitution of swietenine, the non-bitter principle of the seeds of *Swietenia macrophylla* King. Part II.—By Tarakeswar Chakrabartty and Asima Chatterjee (neé Mookerjee) 117
24. Action of Prevost's reagent on $\Delta^{9:10}$-octalin.—By Sukh Dev 121
25. Azulenes and related substances. Part IX. *cyclo*Pentenoazulenes. 1 : 2-Trimethyleneazulene.—By Sukh Dev 126
26. Action of sulphur dioxide water on permanganates of barium and silver.—By Kundan Lal and Chander Mehra 131
27. Chemical studies of some Indian Lauraceae fats. Part I.—By S. A. Narang and S. V. Puntambekar 135
28. Chemical studies of some Indian Lauraceae fats. Part II. The fatty oil from seeds of *cinnamomum camphora* Nees.—By S. A. Narang and S. V. Puntambekar 143
29. Studies on the potentiometric determination of ascorbic acid in fruit and vegetable extracts.—By G. Sitaramaiah 147

Short Notes:

Atomic and structural rheochors.—By R. P. Shukla 150
Detection of cobalt by *o*-phenylenediamine.—By R. L. Dutta 151

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY
92, UPPER CIRCULAR ROAD, CALCUTTA 9.

READY DELIVERY

"SIGCOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

"SELECTA" BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETERS

SPECTROPHOTOMETER

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTICAL BALANCE

CAPACITY : 200 Gms.

SENSITIVITY : $\frac{1}{10}$ Mgm.

5 Divisions throw of pointer for addition of 1 Mgm.

CARL-ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

HERAEUS- OVENS

JULIUS PETER- BOMB CALORIMETER

HOPPLER- VISCOMETERS

Distributors :

ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.

CALCUTTA MADRAS BOMBAY NEW DELHI

Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.

2. A paper will not normally be considered for publication in the Journal unless at least one of the authors or authors is (are) either a Fellow or an Associate member of the Society.

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. All papers should be submitted in typescript with double line and marginal spacings. Tables and foot-notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. All papers should be carefully revised and should be absolutely in final form of printing. Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm., c.c., ml., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenever possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline); year of publication; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.*, 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "Found:———; ———. ——— requires ——— per cent". Analytical results for compounds which have been previously known should be given in the form: "Found:——; ———. Calc. for———: ———; ——."

12. Every paper should be accompanied by a short abstract giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the nvestigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, which should be returned whithin a week to the Hony. Secretary, failing which it will be directly printed.

14. Authors will get 50 copies of reprints free of charge and exxtra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs. It would be desirable to inform him when the manuscript is sent.

15. **Notes will be given priority in publication.**

Change of address should be immediately intimated to the office.

No claims will be allowed for copies of Journal lost in the mail or otherwise, unless such claims are received within 90 days of the date of issue.

	Inland rates.	Foreign rates.	
		Sterling area	Dollar area
Cost of Single Issue	**Rs. 3**		
Annual Subscription	**,, 20 (for Fellows)**	**20**	**25**
	,, 24 (for Subscribers)	**28**	**32**
	,, 28 (Composite)	**34**	**40**

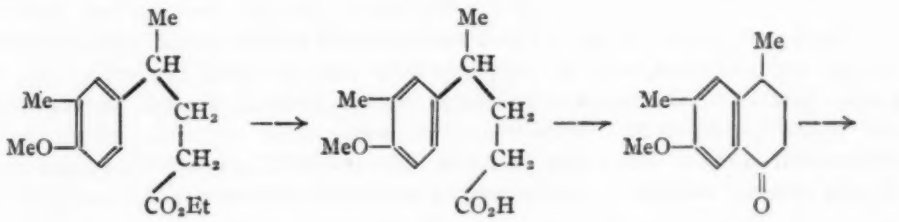
[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

FRIEDEL-CRAFTS' REACTION INVOLVING UNSATURATED KETONES AND ESTERS. PART VII. ALKYLATION OF *o*- AND *p*-CRESOL METHYL ETHERS WITH ETHYL ALLYLACETATE AND ALLYLACETONE

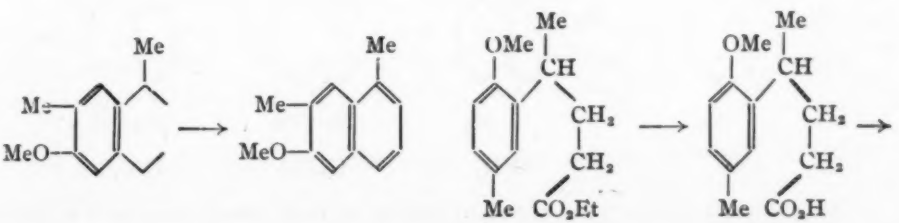
By O. P. Vig, S. S. Sandhu and S. M. Mukherji

Aluminium chloride-catalysed reaction of ethyl allylacetate and allylacetone with *ortho*- and *para*-cresol methyl ethers has been studied, the condensation products serving as readily accessible intermediates in the synthesis of naphthalene derivatives. The reaction with allylacetone is accompanied *in situ* with cyclodehydration, rendering the approach to naphthalene derivatives still simpler.

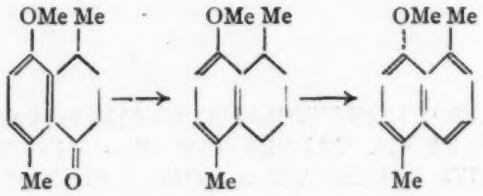
In Part VI (this *Journal*, 1957, **34**, 9) we reported the results of aluminium chloride-catalysed reaction of ethyl allylacetate and allylacetone with anisol. We also recorded therein the facile cyclodehydration undergone by the product from anisol and allylacetone giving rise to a still simpler route to naphthalene derivatives. The present communication describes the cationoid reaction of ethyl allylacetate and allylacetone with *ortho*- and *para*-cresol methyl ethers. Following the conditions described in the case of anisol (Part VI, *loc. cit.*) they gave with ethyl allylacetate, under the influence of anhydrous aluminium chloride, (I) and (VI) in 43 and 40% yields respectively. These esters were hydrolysed and cyclised through Johnson's inverse addition technique to the corresponding ketones (III) and (VIII), which were reduced and dehydrogenated to the respective naphthalene derivatives, (V) and (X), essentially according to the conditions laid down in the case of anisol (*loc. cit.*).



(I) (II) (III)

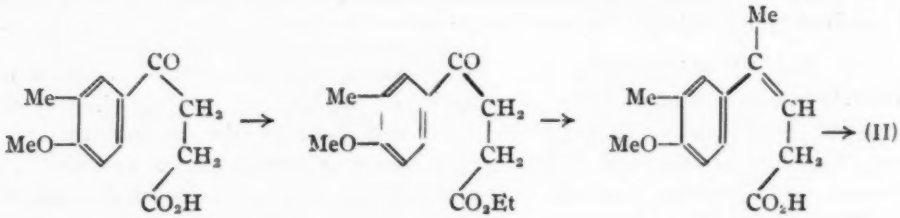


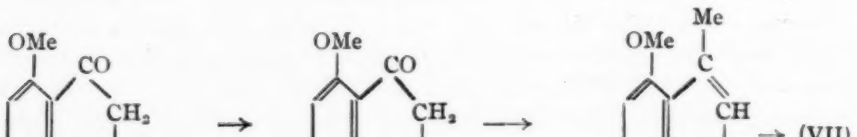
(IV) (V) (VI) (VII)



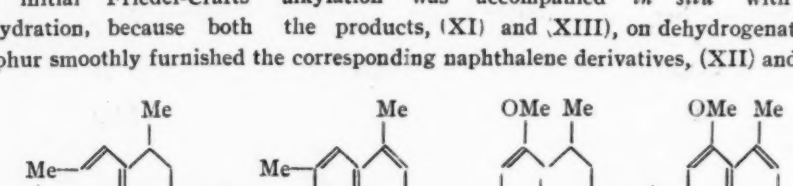
(VIII) (IX) (X)

The orientation of the substituents in the products (I) and (VI) has been proved by independent and unambiguous synthesis of the corresponding acids, (II) and (VII), according to the following schemes :





Cresol methyl ethers (*o*- and *p*-) were then subjected to aluminium chloride-catalysed reaction with allylacetone at 0°-5°, exactly as in the case of anisol (*loc. cit.*). But in neither case could the expected ketonic products be isolated. Instead, we found that the initial Friedel-Crafts alkylation was accompanied *in situ* with cyclo-dehydration, because both the products, (XI) and (XIII), on dehydrogenation with sulphur smoothly furnished the corresponding naphthalene derivatives, (XII) and (XIV).



(XI) (XII) (XIII) (XIV)

The enhanced tendency to cyclodehydration in these cases, in contrast to anisol (*loc. cit.*), can be explained on the basis of enhanced nucleophilicity of the aromatic

substrates. This is borne out by the increased yields, by about 10%, of the products of Friedel-Crafts' alkylation with ethyl allylacetate, when compared with that from anisol.

EXPERIMENTAL*

Ethyl γ-(3-Methyl-4-methoxyphenyl)-valerate (I).—Freshly distilled *o*-cresol methyl ether (75 c.c.) was allowed to react with ethyl allylacetate (20 g.) in presence of anhydrous aluminium chloride (40 g.), following the direction of Mukherji *et al.* (*J. Org. Chem.*, 1953, **18**, 1499), and after working up the reaction mixture in the usual manner, 15 g. (43%) of ethyl γ-(3-methyl-4-methoxyphenyl)-valerate (I), b.p. 140-45°/7 mm., was obtained. (Found: C, 71.68; H, 8.90. $C_{15}H_{22}O_3$ requires C, 71.97; H, 8.86%).

γ-(3-Methyl-4-methoxyphenyl)-valeric Acid (II).—The above ester (13 g.) was hydrolysed by refluxing with alcoholic caustic potash solution (KOH 8 g., water 5 c.c. and alcohol 165 c.c.) on the water-bath for 6 hours. The acid (II) was isolated in the usual way in 80% yield, boiling at 176-78°/6 mm. (Found: C, 69.86; H, 8.02. $C_{13}H_{18}O_3$ requires C, 70.24; H, 8.10%).

The *S-benzylisothiouronium salt* of the acid (II) was prepared in the prescribed manner and was crystallised from dilute alcohol, m.p. 119°. (Found: N, 7.49. $C_{21}H_{28}O_3N_2S$ requires N, 7.21%).

4:6-Dimethyl-7-methoxy-1-tetralone (III).—The acid (II: 10 g.) in dry benzene (25 c.c.) was converted into its acid chloride by PCl_5 (10 g.) in the usual way. The acid chloride without being isolated was cyclised by $AlCl_3$ (anhyd., 7 g.), following the condition laid down by Mukherji *et al.* (*loc. cit.*) for the preparation of 4:6-dimethyl-1-tetralone, when 8 g. (80%) of the ketone (III) was obtained, b.p. 140-43°/8 mm. (Found: C, 76.30; H, 7.84. $C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%).

The *2:4-dinitrophenylhydrazone* of the above ketone was prepared by the sulphuric acid method and was crystallised as red flakes from ethyl acetate, m.p. 213°. (Found: N, 14.4. $C_{19}H_{20}O_5N_4$ requires N, 14.58%).

1:7-Dimethyl-6-methoxy-tetralin (IV).—The above ketone (7 g.) was refluxed with a mixture of amalgamated zinc (50 g.), toluene (50 c.c.), glacial acetic acid (1 c.c.), HCl (conc., 90 c.c.) and water (40 c.c.) for 32 hours in the oil-bath at 130-40°. Every six hours 5 c.c. of HCl (conc.) was added. The reaction mixture was worked up in the usual way when 6 g. (95%) of the tetralin derivative (IV) was obtained, b.p. 135-36°/5 mm. (Found: C, 82.32; H, 9.23. $C_{13}H_{18}O$ requires C, 82.10; H, 9.47%).

1:7-Dimethyl-6-methoxynaphthalene (V).—The above tetralin (3 g.) was heated with sulphur (1.25 g.) at 180-90° for 6 hours, and the reaction product was steam-distilled. The distillate after working up in the usual way gave 1.5 g. (50%) of the naphthalene derivative (V), b.p. 130-32°/2 mm. (Found: C, 83.64; H, 7.39. $C_{13}H_{14}O$ requires C, 83.83; H, 7.58%).

The *picrate* was prepared in the usual manner and was crystallised from alcohol as red crystals, m.p. 144°. (Found: N, 9.90. $C_{19}H_{17}O_8N_3$ requires N, 10.12%

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

Ethyl γ-(2-Methoxy-5-methylphenyl)-valerate (VI).—Freshly distilled *p*-cresol methyl ether (100 g.) was subjected to the aluminium chloride-catalysed reaction with ethyl allylacetate (20 g.) under the same conditions of temperature and catalyst concentration as described in the case of (I), when 14 g. (40%) of the ester (VI) was obtained, b.p. 135-38°/6 mm. (Found: C, 71.75; H, 8.93. $C_{15}H_{22}O_3$ requires C, 71.97; H, 8.86%).

γ-(2-Methoxy-5-methylphenyl)-valeric Acid (VII).—The above ester (14 g.) was hydrolysed by refluxing with alcoholic caustic potash solution (KOH 9 g., water 5 c.c. and alcohol 160 c.c.) for 14 hours on the steam-bath. After working up in the usual way, 9 g. (72%) of the acid, (VII), crystallised from petroleum ether (80°-100°), m.p. 94°, was obtained. (Found: C, 70.19; H, 8.24. $C_{13}H_{18}O_3$ requires C, 70.24; H, 8.10%).

The S-*benzylisothiouronium* derivative was prepared in the usual manner and was crystallised from dilute alcohol, m.p. 119-20°. (Found: N, 6.85. $C_{21}H_{28}O_3N_2S$ requires N, 7.21 %).

4:8-*Dimethyl-5-methoxy-1-tetralone* (VIII).—The cyclisation of the acid (VII: 9 g.) was accomplished through its acid chloride which was obtained by treatment with PCl_5 (9.5 g.). When treated with aluminium chloride (6.5 g.) as in the case of (II), 5.3 g. (67%) of the ketone (VIII) was obtained, distilling at 150-53°/7 mm. (Found: C, 76.52; H, 7.83. $C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%).

The *semicarbazone* of (VIII) was prepared in the usual manner and was crystallised as a colorless mass from dilute alcohol, m.p. 157°. (Found: N, 16.30. $C_{14}H_{19}O_2N_3$ requires N, 16.10%).

The 2:4-*dinitrophenylhydrazone* was prepared by sulphuric acid method and was crystallised from ethyl acetate as red needles, m.p. 224° (decomp.). (Found: N, 14.2. $C_{19}H_{20}O_5N_4$ requires N, 14.58%).

1:5-*Dimethyl-8-methoxy-1:2:3:4-tetrahydronaphthalene* (IX).—The above ketone (VIII: 5 g.) was refluxed for 36 hours with a mixture of amalgamated zinc (35 g.), toluene (30 c.c.), glacial acetic acid (1 c.c.), HCl (conc., 60 c.c.) and water (25 c.c.) in the oil-bath at 130-40°. After working up in the usual way 3.1 g. (67%) of the desired product (IX) was obtained as a colorless oil, b.p. 120-22°/3 mm. (Found: C, 82.00; H, 9.32. $C_{13}H_{18}O$ requires C, 82.10; H, 9.47%).

1:5-*Dimethyl-8-methoxynaphthalene* (X).—The above tetralin (IX: 2.5 g.) was heated with sulphur (1 g.) at 180-90° for 6 hours, when after the usual working up, 1.6 g. (64%) of pure (X) was obtained (distilled over sodium metal), b.p. 120-24°/2 mm. (Found: C, 83.57; H, 7.45. $C_{13}H_{14}O$ requires C, 83.83; H, 7.58%).

The *picrate* was prepared in the customary fashion and was crystallised from alcohol, m.p. 161°. (Found: N, 10.40. $C_{19}H_{17}O_8N_3$ requires N, 10.12%).

1:4:7-*Trimethyl-6-methoxy-1:2-dihydronaphthalene* (XI).—*o*-Cresol methyl ether (75 g.) was treated with allylacetone (12.5 g.) in presence of anhydrous aluminium chloride (25 g.) under the same condition as in the case of (I) except that the temperature was never allowed to go beyond 5°, when 11 g. (40%) of (XI), b.p. 116-20°/4 mm., was obtained. (Found: C, 83.00; H, 8.73. $C_{14}H_{18}O$ requires C, 83.16; H, 8.91%).

1 : 4 : 7-*Trimethyl*-6-*methoxynaphthalene* (XII).—The above product (XI : 5 g.) was heated with sulphur (1 g.) for 5 hours at 180-90°. On working up, the reaction mixture gave 3 g. (60%) of the naphthalene derivative (XII), m.p. 80° (crystallised from methyl alcohol). (Found : C, 83.6 ; H, 7.99. $C_{14}H_{16}O$ requires C, 84.0 ; H, 8.0%).

The *picrate* was prepared in the usual way and was crystallised from alcohol as red plates, m.p. 139-40°. (Found : N, 9.36. $C_{20}H_{19}O_8N_3$ requires N, 9.79%).

1 : 4 : 5-*Trimethyl*-8-*methoxy*-1 : 2-*dihydronaphthalene* (XIII).—*p*-Cresol methyl ether (50 g.) was acted upon with allylacetone (10 g.) in the same way as described in the preparation of (I), the temperature being kept between 0° and 5°. After working up in the usual manner, 9 g. (41%) of the product (XIII) was obtained, b.p. 120-22°/5 mm. (Found : C, 83.23 ; H, 8.76. $C_{14}H_{18}O$ requires C, 83.16 ; H, 8.91%).

1 : 4 : 5-*Trimethyl*-8-*methoxynaphthalene* (XIV).—The dihydronaphthalene (XIII : 5 g.) was heated with sulphur (1 g.) for 5 hours at 183-90°, when 3.3 g. (66%) of the above naphthalene (XIV) was obtained as a colorless liquid on distillation over sodium metal, b.p. 135-38°/6 mm. (Found : C, 84.12 ; H, 8.32. $C_{14}H_{16}O$ requires C, 84.0 ; H, 8.0%).

The *picrate* was prepared in the usual way and was crystallised from alcohol as red plates, m.p. 150°. (Found : N, 10.10. $C_{20}H_{19}O_8N_3$ requires N, 9.79%).

An Unambiguous Synthesis of the Acid (II).—β-(3-Methyl-4-methoxybenzoyl)-propionic acid (40 g.), prepared according to the direction of Desai and Wali (*Proc. Ind. Acad. Sci.*, 1937, **6A**, 144), was esterified by refluxing with a mixture of absolute alcohol (400 c.c.) and H_2SO_4 (conc., 24 c.c.) on the water-bath for about 14 hours. After working up in the usual manner, 35 g. of the ester was obtained (crystallised from alcohol).

This ester (35 g.) was then treated in the cold with methylmagnesium iodide (prepared from 32 g. of MeI and 4.7 g. of Mg) in 125 c.c. of dry ether. After standing for an hour, the mixture was refluxed on the water-bath for about 3 hours and was then decomposed with iced HCl and extracted with ether. The ether extract was washed with 5% Na_2CO_3 solution and the alkaline washings were acidified with dilute HCl. The separated oil was taken up in ether and worked up in the usual manner when 28 g. of γ-methyl-γ-(3-methyl-4-methoxyphenyl)-vinylacetic acid was obtained which without purification was refluxed with 225 g. of HI (*d* 1.7) and 23 g. of red phosphorus at 130-40° for about 16 hours. After working up in the usual way 10 g. of the reduced but demethylated acid was obtained which could not be distilled without charring. Therefore the crude product was directly methylated with dimethyl sulphate (15 g.) in presence of 10% NaOH (50 c.c.). The product obtained was separated and was then hydrolysed with 10% NaOH solution (50 c.c.) by heating on the water-bath for 4 hours. After extracting once with ether, the alkaline aqueous layer was acidified and worked up in the normal way, when the acid (II) (6 g.) distilled at 176-79°/7 mm.

The S-*benzylisothiouronium* derivative of this acid (II) was prepared in the usual fashion and was crystallised from dilute alcohol, m.p. 118°. The m.p. remained

undepressed on admixture with the *S*-benzylisothiouronium salt of the acid (II), obtained through the Friedel-Crafts alkylation of *m*-cresol methyl ether with ethyl allylacetate.

An Unambiguous Synthesis of the Acid (VII).—β-(2-Methoxy-5 methylbenzoyl)-propionic acid (30 g.), prepared according to the direction of Desai and Wali (*loc. cit.*), was esterified by refluxing with a solution of alcohol (300 c.c.) and H_2SO_4 (conc., 18 c.c.) for 12 hours on the water-bath. After working up in the usual way, 26 g. of the corresponding ester was obtained as a colorless oil, b.p. 172-74°/5 mm.

This ester (25 g.) was then treated in the cold with methylmagnesium iodide (prepared from 3.6 g. of Mg and 22 g. of methyl iodide) in ether (100 c.c.). The reaction mixture after standing for about 4 hours was refluxed for 2 hours on the water-bath and then decomposed with ammonium chloride solution. The ethereal layer was extracted with 5% Na_2CO_3 solution and the alkaline aqueous extract acidified with dilute HCl, when γ-methyl-γ-(2-methoxy-5-methylphenyl)-vinylacetic acid (20 g.) was obtained as a clear oil which without purification was reduced by refluxing for 15 hours with a mixture of red phosphorus (16 g.) and HI (*d* 1.7, 160 g.). The product was worked up in the usual way when the demethylated reduced acid (10 g.) was obtained which could not be distilled. This phenolic acid (10 g.) was directly methylated by treatment with dimethyl sulphate (15 g.) in alkaline solution (50 c.c. of 10% NaOH solution). The separated oil was then hydrolysed with 10% NaOH solution (50 c.c.) on the water-bath for 4 hours. The reaction mixture was extracted with ether and alkaline aqueous layer acidified with dilute HCl, when 4 g. of the acid (VII) was obtained. This was crystallised from petroleum ether (80-100°), m.p. 94°. The melting point remained undepressed on admixture with the sample of (VII), obtained previously through the Friedel-Crafts' alkylation of *p*-cresol methyl ether with ethyl allylacetate.

CHEMISTRY DEPARTMENT,
PANJAB UNIVERSITY,
HOSHIARPUR.

Received July 28, 1956.

]Jour. Indian Chem Soc., Vol. 34, No. 2, 1957]

STUDIES IN THE CHEMISTRY OF TELLURIUM. PART I. THE BEHAVIOUR OF TELLURIUM ON CATHODIC AND ANODIC POLARISATION

By H. Khalifa and I. M. Issa

The behaviour of the massive tellurium electrode on cathodic, followed by anodic polarisation, has been studied in 0.1*N*-H_2SO_4, in buffer solutions of p_H 4.98 and 7.02 and in 0.1 *N*-NaOH. The curves exhibit initial jumps in potential without showing breaks, both on anodic and cathodic polarisation before passing to regions of constant potentials. The potentials at the plateaus of the cathodic and the anodic regions and also the decay potentials vary with p_H and current density. The Tafel lines constructed from time—potential curves possess higher slopes than those directly measured. The Tafel lines obtained in 0.1*N*-H_2SO_4 possess two slopes amounting to ~ 0.04 and 0.07 to 0.118 v, indicating that the evolution of hydrogen is governed by an electrochemical mechanism. Anions have no effect on the Tafel line slopes at low current density.

In a previous investigation we studied the behaviour of chromium metal on cathodic, followed by anodic polarisation. Such a study reveals that chromium possesses a large tendency to assume the passive condition, especially on applying the anodic current (Issa, Ammar and Khalifa, *J. Phys. Chem.*, 1955, **59**, 492). It was also found that the behaviour of tellurium in buffer solutions, initially free from the metal ions, can be correlated with the tendency of the element to show signs of passivation (Tourky *et al.*, unpublished). The aim of the present investigation is to study the behaviour of tellurium on cathodic and anodic polarisation with a view to throwing more light on the problem. We also investigated the hydrogen overpotential on tellurium cathodes in sulphuric acid solutions of different concentrations and in buffer solutions of different p_H.

Experimental

Solutions.—The time—potential curves were traced in the course of cathodic and anodic polarisation in 0.1 *N*-H_2SO_4, in buffer solutions of p_H 4.98 and 7.02 and in 0.1 *N*-NaOH solution.

The Tafel lines were constructed in H_2SO_4 solutions ranging from 5 *N* to 0.01 *N*, in buffer solutions covering the p_H range 3 to 12 and in 0.1*N*-NaOH solution of p_H 12.95.

H_2SO_4 solutions were prepared from the Analar product by appropriate dilutions with twice distilled water. Their concentrations were checked by the aid of a standard sodium carbonate solution. The buffer solutions of Clark and Lubs of p_H 3 to 9 and the Ringer buffer of p_H 12 were prepared as recommended by the respective authors and checked for their p_H values by the hydrogen electrode. The NaOH solution was prepared from a carbonate-free, highly concentrated solution by dilution with CO_2-free water and its p_H value estimated by the hydrogen electrode. The solutions were prepared from the Analar products by dissolving in water, twice distilled from alkaline permanganate.

Electrodes.—These were prepared from tellurium rods of 0.8 cm. in diameter provided by Scherring-Kahlbaum. A circular groove and two lateral ones were made at a distance of 1 cm from one end. A platinum wire was fitted well into the circular groove with its ends passing through the lateral ones. The end of the rod was then squeezed into a glass cup above which the platinum ends were sealed to the glass. Electrical contact was maintained through mercury and a copper wire. The apparent surface area of the electrode amounted to ~ 8 cm^2. This was limited by making a circular groove around the rod at a distance of 3 cm from its lower end and dipping the electrode into the solution just to the groove. Before immersion, the electrode surface was rubbed by very fine emery paper, followed by filter paper, when it acquired a highly polished and smooth appearance.

Electrolysis Cell.—This was essentially similar to that of Bockris and Potter (*J. Electrochem. Soc.*, 1952, **99**, 169; *J. Chem. Phys.*, 1952, **20**, 614).

Procedures.—(*A*). The time—potential curves were constructed by using current densities ranging from 5×10^{-6} to 4×10^{-5} amps/cm^2. Prior to polarisation the electrode was left in contact with the solution, freed from oxygen by bubbling through it pure hydrogen, for a period of 30 minutes which was found sufficient for the attainment of thermal and electrochemical equilibrium. The polarisation process consisted in admitting the cathodic current for a period of 60 minutes till the attainment of constant potentials. The potential was then allowed to decay for a period of 30 minutes at the end of which the anodic current was applied. After 30 minutes the polarisation was stopped and the potential allowed to decay once more for a period of 30 minutes.

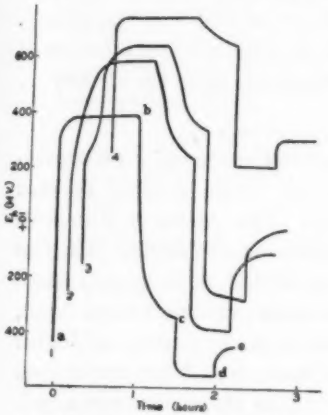
(*B*). For constructing the Tafel lines, the solutions were pre-electrolysed (Azzam *et al.*, *Trans. Faraday Soc.*, 1950, **46**, 918) for a period of 20 hours using a current amounting in the average to 5 ma at the platinum electrode, followed by one-hour electrolysis at the tellurium electrode. The same results were obtained by carrying out the electrolysis for 10 hours, but for the sake of certainty the longer period was preferred. In tracing the Tafel lines, current densities ranging from 1×10^{-5} to 6×10^{-4} amps/cm^2 were applied. After constructing the Tafel lines from higher to lower currents, the p_H's of the solutions were checked by the aid of a glass electrode except in the case of more concentrated acid solutions for which the p_H was calculated from the concentration using activity coefficients as given by Latimer ("Oxidation Potentials", Prentice Hall, N. Y., 1953, p 354).

(*A*). *The Time-potential Curves.*—Representative time—potential curves at a current density of 4×10^{-5} amps/cm^2 at the p_H values 1.5, 4.98, 7.02 and 12.95 are shown in Fig. 1.

The curves obtained at current densities ranging from 5×10^{-6} to 4×10^{-5} amps/cm^2 in 0.1*N*-H_2SO_4 solution are represented in Fig. 2. These latter curves indicate that the behaviour varies with the current density applied both on cathodic and anodic polarisation. At the lower current densities, the curve is characterised by an initial rapid change to less positive potentials, followed by a less steep one before the attainment of constant values on the negative side of the hydrogen electrode slope. The decay curves exhibit an initial rapid change in potential to more positive values, followed by a less steep one, until they reach the initial potentials set before applying the polarising current.

FIG. 1

Cathodic and anodic polarisation curves of tellurium electrode at diff. p_H at 4×10^{-5} amps/cm².

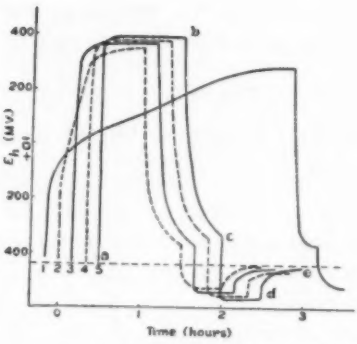


(a-b) cathodic; (b-c) cathodic decay; (c-d) anodic; (d-e) anodic decay.

1—0.1 N-H_2SO_4. 3—p_H 7.02.
2—p_H 4.98. 4—p_H 12.95.

FIG. 2

Cathodic and anodic polarisation curves of tellurium electrode in 0.1 N-H_2SO_4.



(a-b) cathodic; (b-c) cathodic decay; (c-d) anodic; (d-e) anodic decay.

1—C.D. 5×10^{-6} amps/cm². 4—C.D 3×10^{-5} amps/cm².
2— ,, 1×10^{-5}. 5— ,, 4×10^{-5}.
3— ,, 2.5×10^{-5}.

The same behaviour is manifested in the case of anodic polarisation and the decay which follows. The constant potentials attained during the anodic process and after decay are more positive than the initial potentials. A striking phenomenon is that the potentials, set at the constant regions during cathodic and anodic polarisation or cathodic and anodic decay, vary more or less regularly with the current density applied.

At higher current densities (e. g 4×10^{-5} amps/cm²) only a single rapid rise in potential is observed (on cathodic polarisation) before attaining constant potential values at p_H 1.5 and 12.95. The less rapid change, which follows at lower currents, nearly disappears at these latter p_H's and becomes less pronounced at p_H 4.98 and 7.02.

FIG. 3

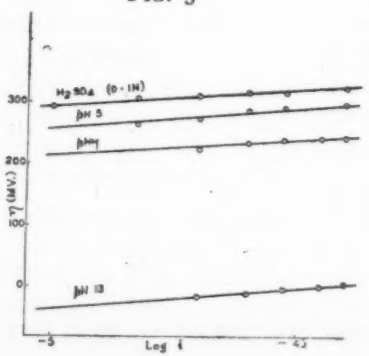
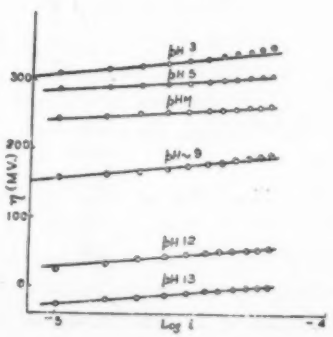


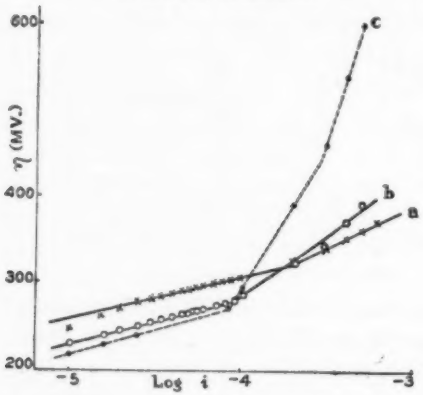
FIG. 4



(*B*). *The Tafel Lines.*—Fig. 3 shows the η—log i curves obtained by plotting the η values obtained at the end of the cathodic polarisation period against log i at p_H values 1.54, 4.98, 7.02 and 12.95. In Fig. 4 are shown the directly measured Tafel lines representing the behaviour in buffer solutions of p_H values 3.05, 4.98, 7.02, 8.92, 11.95 and 0.1 *N*-NaOH of p_H 12.95 within the C.D. range of 1×10^{-5}—6×10^{-5} amps/cm^2. In Fig. 5 are shown representative Tafel lines obtained in sulphuric acid solutions of 2.9, 0.05 and 0.0115 *N*. Tafel lines for other acid concentrations lie in the vicinity of curve a (Fig. 5) and are then not easy to demonstrate.

FIG. 5

Tafel lines directly constructed in H_2SO_4 solutions.



Curves a—c refer respectively to 2.9, 0.05 and 0.1 *N*-H_2SO_4.

The Tafel lines in Figs. 3 and 4 are characterised by a single slope ranging between 0.031 and 0.046. The curves in Fig. 5, on the other hand, show two slopes. The first slope b_1 lying within the C. D. range 1×10^{-5} to 1×10^{-4} amounts to 0.04—0.052 volt, while the second slope b_2 occurs at higher current densities than 1×10^{-4} and varies from 0.07 to 0.1 volt within the acidity range 5 *N* to 0.05 *N*-H_2SO_4 (Table I). Higher slopes amounting to 0.3 volt are obtained in 0.0115 *N*-H_2SO_4 solutions (Fig. 5).

The parameters of the hydrogen overvoltage in the respective solution and the corresponding p_H values are recorded in Table I.

TABLE I

H_2SO_4 conc. (*N*)...	4.89	2.9	0.98	0.49	0.05	0.0115
p_H	0.0097	0.39	0.89	1.14	2.22	2.76
b_1	0.042	0.045	0.046	0.044	0.051	0.052
i_{01}	4×10^{-13}	8×10^{-12}	4.5×10^{-12}	2×10^{-11}	2×10^{-12}	1.5×10^{-9}
a	1.35	1.27	1.24	1.30	1.11	1.10
η at 2×10^{-5} (mv)	273	269	270	273	244	233
b_2	0.074	0.098	0.084	0.07	0.118	0.32
i_{02}	1.6×10^{-9}	1×10^{-8}	3.5×10^{-9}	2.5×10^{-7}	4×10^{-7}	1.2×10^{-5}
a	0.77	0.57	0.69	0.69	0.77	...
η at 5×10^{-5} (mv)	358	361	353	343	391	539

In Table II are listed the parameters of the hydrogen overvoltage in the buffer solutions.

TABLE II

	Buffer solutions					
	HCl + phthalate.	NaOH + phthalate.	NaOH + phosphate	Boric + KCl+NaOH.	NaOH + phosphate.	0.1 *N* – NaOH.
p_H ...	3.05	4.98	7.02	9.29	11.95	12.95
b ...	0.046	0.034	0.031	0.044	0.036	0.038
η at 10^{-5} amps/cm² (mv)	312	288	240	160	28	28
					...	...
a ...	0.95	1.04	1.23	1.84		
$\Delta\eta/\Delta p_H$ ...	12	16	35	50	56	

DISCUSSION

Behaviour in 0.1 *N*-H_2SO_4 *Solution*: *The Time-potential Curves.*—The initial rapid change in potential to more negative values (Fig. 1) is apparently due to an IR drop. In conformity with this fact, the magnitude of the initial rise in potential increases with increasing current density, amounting thus to 200, 270 and 450 mv at 5×10^{-6}, 1×10^{-5} and 2×10^{-5} amps/cm² respectively. The slower change which follows includes reduction of the oxide film, formation of the double layer and the electrodeposition of hydrogen gas on the electrode surface. This latter section of the curve becomes less defined by increasing the current applied and disappears completely when the current amounts to 4×10^{-5} amps/cm². After complete reduction of the oxide film and build up of the double layer, the potential assumes constant values which vary in magnitude with the applied current, indicating that part of this potential is due to an overvoltage effect.

The potential changes which accompany the decay of the cathodic potentials are attributed to the breakdown of the cathodic double layer, the diffusion away or ionisation of hydrogen and the development of the oxide film on the electrode surface. In conformity with this fact, the potential set (+ 0.34 to + 0.37 volt) is intermediate between the values of both oxide and hydride systems, the E_o values of which amount to + 0.53 and − 0.72 volt respectively.

The rapid rise in potential accompanying the application of the anodic current corresponds to further ionisation of hydrogen and formation of the anodic double layer. The less steep change following this part of the anodic curve, which is more pronounced at the lower currents applied (5×10^{-6} and 1×10^{-5} amps/cm²), is due to the deposition of oxygen with subsequent oxidation of the metal. When the electrode surface becomes completely covered with oxide, overlayered by oxygen, the potential assumes constant values which, as in the case of the cathodic potential, vary with the magnitude of the polarising current. This indicates that in both cases a part of the potential is originating from an overvoltage effect.

The decay of the anodic potential is accompained with the collapse of the anodic double layer and the desorption of a certain amount of oxygen doublets before finally passing to a region which lies slightly positive to the metal—metal oxide potential. In this region also, the steady state potential is a function of current density and, as was previously stated, the electrode in its static condition is subject to an oxygen overvoltage effect which is smaller than when the anodic current is applied.

Behaviour in Solutions of different p_H.—In solutions of higher p_H than 1.5 (0.1*N*-H_2SO_4), the relation between current density and the initial drop in potential is the same as in the case of sulphuric acid solution. The slower change which follows becomes also less defined at a C. D. of 4×10^{-5} amps/cm^2 except in the case of p_H 4.98 and 7.02. This may find its origin in the stability of the oxide film within this p_H range, *i.e.* in the vicinity of the iso-electric point of tellurium dioxide (Issa and Awad, *J. Phys. Chem.*, 1954, **58**, 948) which lies at $\sim p_H$ 3.85 owing to the smaller solubility of the dioxide in these solutions as compared with the acid and alkaline ones. In these latter cases, the removal of the oxide is aided by the solvent action of the electrolyte, which is more apparent in the alkali solution. The steady states originating after anodic polarisation lie always more positive to the metal—metal oxide potentials and vary with the magnitude of the current as in the case of sulphuric acid solution. The steady state potentials at the cathodic and anodic regions are not only functions of current density at a given p_H, but like the static potentials and the potentials set after decay, are also function of p_H at a given current density.

The Tafel Lines.—The slope of the Tafel lines within the current density range $1 \times 10^{-5} - 1 \times 10^{-4}$ amps/cm^2 and amounting to 0.04 – 0.045 v indicates that within this current density range the process of hydrogen evolution on tellurium in sulphuric acid solutions of concentrations varying from 5 *N* to 0 5 *N* is governed by an electrochemical mechanism (Bockris *et al.*, *loc. cit.*). Thus, as is well known for an electrochemical mechanism, the slope of the Tafel line is 0.04 and 0.118 v at lower and higher current densities respectively. At higher current densities the slope of the Tafel line lies between 0.07 and 0.118 v, indicating that within this current density range the evolution of hydrogen is governed either by an electrochemical or slow discharge mechanism (Bockris *et al.*, *loc. cit.*).

In dilute sulphuric acid solutions of concentrations less than 0.05 *N*, there appears some resistance overpotential leading to a rapid increase in the value of the slope of the Tafel line above a current density of 8×10^{-5} amps/cm^2. This resistance overpotential is but small at lower current densities where the slope of the Tafel line amounts to 0.05 v.

The Tafel lines obtained in buffer solutions and in 0.1 *N* sodium hydroxide (Table II ; Fig. 5), constructed within the current density range 1×10^{-5} to 6×10^{-5} amps/cm^2, possess the same slopes as in the case of sulphuric acid solutions for the same current density range. This indicates a similar mechanism for the evolution of hydrogen and that anions have no effect on the process of hydrogen evolution. Tafel lines constructed from the time—potential curves by considering the steady state potentials set after one hour (Fig. 3) possess, on the other hand, slopes amounting to 0.052 – 0.07 v, which are higher than the directly traced ones. This is apparently due to the presence of impurities since the solutions were not pre-electrolysed prior to the passage of the current.

Faculty of Science,
Cairo University, Cairo-Giza, Egypt.

Received June 9, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

THE REACTIVITY OF THIOL GROUPS IN PROTEINS. PART III. HUMAN, BOVINE AND HORSE SERUM-ALBUMINS

By R. Lontie and G. Beckers

Specific thiol reagents of different strengths and types were allowed to react on human, bovine and horse serum-albumins, both native and denatured, in 7.5 *M* urea solution. An attempt has been made to interpret the discrepancies observed in the action of the different reagents.

Human, bovine and horse serum-albumins have much in common. A M.W. of 66,000 has somewhat arbitrarily been adopted in our calculations for the three proteins, but for each it corresponds with reliable recent determinations (Edsall, *J. Polymer Sci.*, 1954, **12**, 253).

From physico-chemical investigations, the shape of the three native albumins seems best represented by a prolate ellipsoid with an axial ratio of about 4/1. Determinations for bovine (Oncley *et al.*, *J. Phys. Chem*., 1947, **51**, 184) and horse albumins (Neurath and Saum, *J. Biol. Chem.*, 1939, **123**, 347) point to 145-150 Å for the major axis and 34-38 Å for the minor. One terminal N-group-aspartic acid- has been detected in the three albumins alike, without necessarily implying the presence of a single polypeptide. A complete amino-acid analysis has been made for human and bovine albumins. They indicate a close overall similarity of composition, with a few significant differences. The sequences are surely not identical (Thomson, *J. Biol. Chem.*, 1954, **208**, 565). Analyses of sulphur amino-acids of the three albumins have been made. The % cystine is practically identical (32-34 groups). Cysteine and methionine contents vary: in human albumin there are 4 cysteine and 6 methionine groups/Mol. (Brand *et al.*, *Ann. Rev. Biochem.*, 1947, **16**, 223), in bovine albumin 2.5 (Goebel *et al.*, *J. Exptl. Med.*, 1949, **89**, 479) and 4 (Lewis *et al.*, *J. Biol. Chem.*, 1950, **183**, 23) respectively, and in horse albumin 3 cysteine but no methionine at all (Brand *et al.*, *J. Biol. Chem.*, 1941, **141**, 999). The structure of bovine albumin alone has been studied by X-rays (Riley and Arndt, *Nature*, 1952, **169**, 138). Pauling's α-helixes or a very closely similar pattern would represent correctly the main polypeptidic configuration. From the close similarities of properties, shape and composition of the 3 albumins, it can safely be inferred that all the three are best represented by α-helixes. They contain about 550 amino-acids, including 27-29 proline residues. With 1.5 Å per radical, the molecules are likely to consist of a bundle of the six segments of a helix bent back on itself, closely packed together and eventually intertwined.

Experimental

The methods of determination of the SH groups by silver, *p*-chloromercuribenzoate (*p*-ClHgb), ferricyanide, iodoacetic acid and iodoacetamide have been previously described (this *Journal*, 1956, **33**, 285, 289).

A human serum-albumin preparation of Poviet, Amsterdam, was used. Concentrations were determined on the basis of a % N_2^* of 15.95 (Brand *et al.*, *loc. cit.*, 1947) by

semimicro Kjeldahl. Bovine serum-albumin was prepared by fractional precipitation with alcohol at a low temperature, according to Cohn (*J. Amer. Chem. Soc.*, 1946, **63**, 459). It was homogeneous in the electrophoresis at p_H 8 7 and ionic strength 0.1, but gave one and even two minor components at a lower p_H. A %N of 16.1 was adopted (Lewis *et al.*, *loc. cit.*). Horse serum-albumin was prepared by fractional precipitation with $(NH_4)_2SO_4$ and recrystallised thrice according to Hermans (Thesis, Louven Univ., 1951). It showed two components in equal proportions in the electrophoresis at p_H 7.26 and ionic strength 0.1. A %N of 15.9 was adopted (Neurath *et al.*, *J. Biol. Chem.*, 1941, **138**, 411). Denaturations were performed as described previously (this *Journal*, 1956, **33**, 285). In order to avoid discrepancies arising from differences in the conditions of preparation, for each protein, all the determinations were performed on aliquots of an identical preparation.

TABLE I

[No. denotes number of determinations]

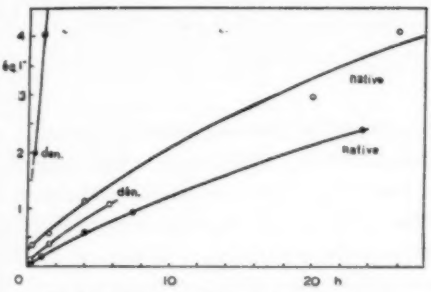
	$Ag(NH_3)_2^+$.		*p*-ClHgb.		$Fe(CN)_6^{4-}$		ICH_2COO^-.	ICH_2CONH_2.
	SH/M.	No.	SH/M.	No.	SH/M (?)	No.	SH/M.	SH/M.
			Human serum-albumin : Native.					
0.4		6	0.05	4	1	3	0	0.3
0.4	Lit. (Benesch, *Arch. Biochem.*, 1948, **19**, 35).							
0.7	(Jensen, *J. Biol. Chem.*, 1950, **185**, 411 ; Weissman, *ibid.*, 1950, **187**, 153).							
			Denatured in urea 7.5 *M*.					
0.2		5	0.2	4	1x	3	0 (?)	0
	x : id after 70 hours of contact urea-protein							
			Bovine serum-albumin : Native.					
0.2		11	0.45	6	1.2	2	0.2	0.2
0	(Rosenberg, *Anal. Chem.*, 1950, **22**, 1186).						(t° = 28°)	
0.7	(Jensen, *loc. cit.* Benesch, *loc. cit.*).							
			Denatured in urea 7.5 *M*					
0.2		3	0.35	8	1.1	1	1.8 (?)	0.6
0	(Rosenberg, *loc. cit.*).						(t° = 28°)	
			Horse serum-albumin : Native.					
0.6		10	0	6	1.2	6	0.5	0.5
			Denatured in urea 7.5 *M*.					
0.1		3	0	6	0.8x	4	...	0.5
	x : id after 24 hours of contact urea-protein.							

Iodoacetamide-iodoacetate

It is impossible to determine by extrapolation a reliable value for the free SH groups, reacting with iodoacetate in the denatured human albumin. It may be surmised however, that this number will be at most equal to the number of SH groups reacting

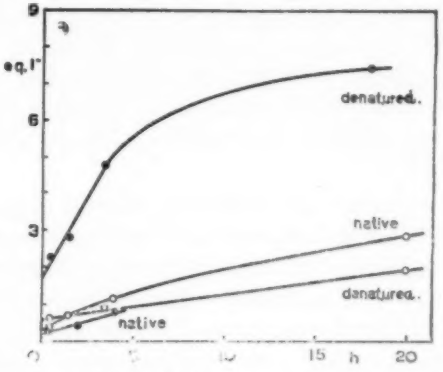
with iodoacetamide in the same protein. The latter has a more rapid reaction with the SH groups than iodoacetate. The SH reaction is completely masked here by other reactions, particularly with the amino groups. The slope of the curve expressing the

FIG. 1



Equivalents of I^- liberated in terms of time, in the reactions of native and urea-denatured human serum-albumin with iodoacetate ( ) and iodoacetamide (o). p_H = 6.96. Temp.° = 25°.

FIG. 2



Equiv. of I^- liberated in terms of time for native and urea-denatured bovine albumin with iodoacetate (•) and iodoacetamide (o). p_H = 6.96. Temp. = 28°. The curves for horse albumin start at o $5I^-$ liberated at time = o, but soon practically coincide with the correspodning curves for the bovine albumin.

liberated iodine in terms of time of reaction between denatured albumin and iodoacetate remains very steep to time = 2 hours ($23I^-$), to become later less and less pronounced (after 24hours : 33 I^-). The reaction of NH_2 groups is much more rapid with iodoacetate than with iodoacetamide, while methionine reactions proceed at sensibly equal speed. We can thus infer from the comparison of the different curves that in a 7.5 *M* urea solution, a large number of NH_2 groups from lysine, amides etc. are unmasked.

The interpretation of these curves calls for remarks identical with those made for human albumin, though the increase of the amino-reaction with iodoacetate brought about by denaturation is here less important. Comparisons of the binding power for methyl orange etc. at different p_H for human and bovine serum-albumins had lead Klotz *et al.* (*J. Phys. Chem.*, 1952, **56**, 77) to similar conclusions.

The values recorded for the *p*-ClHgb reactions are subject to caution. Serum-albumin solutions are slightly yellow and an exact determination of the end-point by the appearance of the rosy colour of the reaction of an excess cysteine with nitroprusside is difficult. Some data from the literature cast a doubt on our data for the human albumin reaction : human albumin first put in contact with *p*-ClHgb gives no reaction with silver (Benesch, *loc. cit.* Weissmann, *loc. cit.*) and two molecules of the mercaptalbumin fraction of human albumin are bound by the bulky bifunctional Hg reagent of Straessle (*J. Amer. Chem. Soc.*, 1951, **73**, 504) to form a dimer. Both human (Hughes, *loc. cit.*) and bovine (Lontie *et al.*, *Arch. Int. Physiol.*, 1951, **62**, 556) albumins form a dimer with Hg.

From its reaction with amandin, we showed that ferricyanide was probably no specific reagent of the SH groups in all proteins (this *Journal*, 1956, **33**, 285) as it was in ovalbumin (Anson, *J. Gen. Physiol.*, 1939, **22**, 247). The determinations on the three serum albumins seem to confirm this finding. It is unlikely that SH groups which fail to react with other oxidising agents, silver and *p*-ClHgb would react with ferricyanide. Besides, denaturation in 7.5 *M* urea does not affect the reaction. After 70 hours of contact between protein and urea, the number of SH groups determined would normally decrease due to the oxidation by air of part of them ; yet, the ferricyanide reaction of denatured human albumin is unaffected. The data seem to indicate the presence of one oxidisable group per molecule, different from the SH, in the three serum albumins, native as well as denatured.

Unlike ovalbumin, denaturation in a 7.5 *M* urea solution does not bring about in the three serum-albumins an increase of the number of reactive SH groups. The change of structure must be less thorough. After denaturation by relatively mild procedures, the α-helix structure remains essentially intact (Riley *et al.*, *Proc. Roy. Soc.*, 1953, **B141**, 93). Physico-chemical data show that denaturation does not bring about a total uncoiling, but rather an expanding of the serum-albumin molecule (Birefringence: Foster *et al.*, *J. Amer. Chem. Soc.*, 1954, **76**, 6044. Viscocity and diffusion: Neurath and Saum, *loc. cit.*). The protein keeping the shape of an ellipsoid, the major axis would be doubled while the minor axis would become about 20 Å (Neurath and Saum, *J. Biol. Chem.*, 1939, **128**, 347 ; 1941, **138**, 411 ; 1942, **142**, 249). Things happen as if, in the bundle of 6 helixes, 2 subunits of three closely interconnected helixes (Pauling's three stranded ropes?) were more loosely bound together by electrostatic forces and hydrogen bonds. Hence, the great sensitivity to p_H and ionic strength or such low concentrations of urea as 2*M*. The protein would open or split lengthwise by the repulsion of the two subunits, which at the limit would separate by rotation around the peptide linking the two subunits (Harrington *et al.*, *Biochem. J.*, 1956, **62**, 569). This hypothesis would explain that SH groups masked in the native albumin could remain so after denaturation, and that other groups, present in large numbers, eventually engaged in some interhelix bonds in the native albumin, would become easily accessible to their reagents, as denaturation proceeds. Such are the numerous amino groups reacting easily with iodoacetate and binding a larger number of organic anions after denaturation (Klotz, *Cold Spring Harbour Symp. Quant. Biol.*, 1950, **14**, 97). Literature shows an instance of a similar increase in the availability of disulphide groups (Neurath and Saum, *loc. cit.*, 1939). Tyrosine (Klotz, *Disc. Faraday Soc.*, 1953, No. 13, 189) and amino groups (Hermans, *loc. cit.*) become available in increasing numbers with increasing p_H on the alkaline side.

A decrease is observed in the silver reactions of human (0.25 instead of 0.45 SH/M) and horse (0.1 instead of 0.6 SH/M) albumins after denaturation. Bovine (0.2 instead of 0.5 SH/M) and horse (0.1 instead of 0.5 SH/M) denatured albumins have a smaller number of SH groups reacting with silver than with iodoacetamide. This could be explained by a spontaneous oxidation by air at the higher p_H (9.25/7) : of the silver reaction as in the case of ovalbumin (this *Journal*, 1956, **33**, 289). Such oxidations, however, seem to

imply here the formation of intermolecular disulphide bonds. This possibility should not be ruled out and is advocated by Huggins *et al.* (*Nature*, 1951, **167**, 592) to explain gel formation in 5 5 *M* urea solutions of bovine albumin, while Robert *et al.* (*Disc. Faraday Soc.*, 1953, No. 13, 49) observed an oxidation by air of the SH groups of horse albumin at high p_H. Ammonium ions could also affect unfavourably the SH titration (Greenstein and Edsall, *ibid.*, 1940, **133**, 397). The new method of Benesch *et al.* (*J. Biol. Chem.*, 1955, **216**, 663), using the *tris*- (hydroxymethyl)-aminomethane-silver complex instead of the NH_3 one, allows to work at neutrality and to observe an increase in reacting SH groups upon denaturation by urea (from 0.67 to 1.04 SH/M).

Differences of reactivity of the SH groups of identical serum-albumins with different reagents can be explained by the same reasons advocated in the case of ovalbumin (Lontie *et al.*, *loc cit.*).

From the reactions of Hg on serum-albumins, only one component of the heterogeneous albumins in the native state seems to posses a reactive SH group : the "mercaptalbumin" (Hughes *et al.*, *loc. cit.*, *et seq*). This explains why the number of available SH groups in serum-albumins is not expressed by even an approximate small integer. The proportion in which mercaptalbumin is present in each sample could explain differences observed between literature data for silver titrations of the same albumin, prepared according to different methods. Fully significant comparisons call for a fractionation of the components of the serum-albumins prior to the determination of their SH groups.

LABORATORY OF BIOCHEMISTRY,
LOUVAIN UNIVERSITY, BELGIUM,
&
ST. XAVIER'S COLLEGE,
CALCUTTA-16.

Received June 18, 1956.

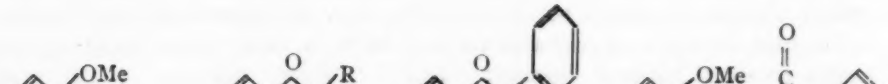
[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART X. 2-PHENYLCOUMARONES

By J. N. Chatterjea and S. K. Roy

A simple method of preparation of 2-phenylcoumarones from *o*-methoxybenzyl aryl ketones of the type (I) is described.

A remarkably simple method of preparation of 2-phenylcoumarone (II: R=Ph) in an excellent yield has been achieved by boiling α-cyano-α-(*o*-methoxyphenyl)-acetophenone (I: R=Ph) with hydrobromic acid in acetic acid. This involves completion of four stages, viz., hydrolysis, decarboxylation, demethylation and cyclisation, in one operation.



(I) (II) (III) (IV)

Several 2-phenylcoumarones have been prepared by this simple procedure; these are collectively described in Table Ib. 2-Benzylcoumarone (Stoermer *et al.*, *Ber.*, 1924, **57**, 72) has been prepared similarly from the cyano-ketone (I: R=$PhCH_2$). When the compound (I: R=2-OMe.C_6H_4) was similarly treated with hydrobromic acid, the product was a mixture of 2-(*o*-hydroxyphenyl)-coumarone and the furo-coumarin (III). The latter has the same skeleton as tri-*o*-methylwedelolactone, a natural product derivative (Govindachari *et al.*, *J. Chem. Soc.*, 1956, 629).

In an attempt to prepare 2-(*o*-carboxyphenyl)-coumarone, required in another investigation, the keto-nitrile (I: R = 2-ethoxycarbonylphenyl) was prepared from *o*-methoxyphenylacetonitrile and ethyl phthalate. The required coumarone was, however, not obtained from it by this method, possibly because of the facile formation of the phthalide (IV), which has been isolated.

Experimental *

2-Phenylcoumarone.—A mixture of the cyano-ketone (I: R=Ph ; Chatterjea, this *Journal*, 1956, **33**, 447) (0.6 g.), acetic acid (7 c.c.) and hydrobromic acid (7 c.c., 48%) was heated in an oil-bath (150-60°) for 3 hours. The mixture was poured into water and the precipitated 2-phenylcoumarone (0.4 g.) crystallised from alcohol, The com-

* All m.p.s are uncorrected.

pound was obtained in colorless plates, m.p. 120-21° (lit., m.p. 120°). (Found : C, 87.0; H, 5.2. Calc. for $C_{14}H_{10}O$: C, 86.6 ; H, 5.2%). The compound dissolved in sulphuric acid with a yellow colour which turned green immediately.

2-Benzylcoumarone.—A solution of *o*-methoxyphenylacetonitrile (4.4 g. Baker *et al., J. Chem. Soc.*, 1953, 1386) and ethyl phenylacetate (5.0 g.) in benzene (20 c.c.) was added to dry sodium ethoxide (sodium, 0.7 g.) and refluxed for 2 hours. The *sodium salt* of the keto-nitrile (I : R = $PhCH_2$) (6.9 g.) separating was collected, washed with dry ether, dissolved in water and acidified. The *keto-nitrile* was obtained in colorless prisms from methanol, m.p. 96°. (Found : C, 77.4 ; H, 5.7. $C_{17}H_{15}O_2N$ requires C, 76.9 ; H, 5.7%). This nitrile (2.0 g.) was refluxed for 9 hours with a mixture of acetic acid (20 c.c.) and HBr (20 c.c.). The product, isolated with ether, was washed with alkali, dried and distilled. 2-Benzylcoumarone was obtained as a colorless oil (1.2 g.), b.p. 174°/8.5 mm. (Stoermer *et al.*, record b.p. 180-85°/15 mm). (Found : C, 86.4 ; H, 5.6. Calc. for $C_{15}H_{12}O$: C, 86.5 ; H, 5.8%). The compound gave a pink coloration with sulphuric acid.

Benzofuro-(2′ : 3′ : 3 : 4)-coumarin.—Equimolecular quantities of *o*-methoxyphenylacetonitrile and ethyl *o*-methoxybenzoate were refluxed in dry benzene solution with freshly prepared sodium ethoxide (1 *M*) for 5 hours. The *keto-nitrile* (I : R = 2-OMe.C_6H_4) crystallised from alcohol in colorless prisms, m.p. 112°. (Found : C, 72.4 ; H, 5.3 ; N, 5.2. $C_{17}H_{15}O_3N$ requires C, 72.6 ; H, 5.3 ; N, 5.0%). The nitrile (1.7 g.) was refluxed with a mixture of acetic acid (9 c.c.) and HBr (9 c.c.) for 3 hours. The mixture was poured into water and cooled overnight in a refrigerator. The solid on crystallisation from acetic acid gave the *furo-coumarin* (III) in bluish prismatic needles, m.p. 180-81°, yield 0.15 g. (Found : C, 76.1 ; H, 3.5. $C_{15}H_8O_3$ requires C, 76.2 ; H, 3.3%).

The compound responds to no ferric reaction and is insoluble in dilute alkali. The acetic acid mother-liquor was treated with water and the precipitated product extracted with dilute alkali, filtered and acidified. *2-(2′-Hydroxyphenyl)-coumarone* was obtained in colorless prisms from acetic acid, m.p. 95°, developing a green coloration with H_2SO_4. (Found : C, 80.2 ; H, 5.0. $C_{14}H_{10}O_2$ requires C, 80.0 ; H, 4.8%).

Condensation of Ethyl Phthalate with o-Methoxyphenylacetonitrile.—Ethyl phthalate (4.4 g.) was condensed with the nitrile (3.0 g.) in the presence of dry sodium ethoxide (sodium, 0.47 g.) as before. The resulting *keto-nitrile* (I : R = 2-ethoxycarbonylphenyl) which had no tendency to crystallise was boiled with a mixture of acetic acid and HBr (10 c.c. each) for 8 minutes. The gummy product, obtained on pouring into water, solidified in contact with alcohol. The *phthalide* (IV) on two crystallisations from alcohol was obtained in golden yellow flat needles, m.p. 159-60°, dissolving in sulphuric acid with a light colour. [Found : C, 73.7, 73.7 ; H, 4.0, 4.0 ; N, 5.3; OMe, 10.7. $C_{17}H_{11}O_3N$ requires C, 73.6 ; H, 4.0 ; N, 5.1 ; OMe (1), 11.2%].

In Table IA are described some of the keto-nitriles obtained by the condensation of *o*-methoxyphenylacetonitrile with substituted benzoic esters and the 2-phenylcoumarones derived from these nitriles are shown in Table IB.

TABLE I

No.	Substituent.	Solvent of cryst.	Cryst. shape.	Yield.	M.P.	Mol. formula.	Found.	Calc.
			A. Keto-nitriles (I).					
1.	R = $C_6H_4CH_3$ (*p*)	Acetic acid-alcohol	Colorless prisms	70%	109-10°	$C_{17}H_{15}O_2N$	N : 5.2%	5.3%
2.	R = $C_6H_4CH_3$ (*m*)	Acetic acid	Do	68	71-72°	$C_{17}H_{15}O_2N$	N : 5.0	5.3
3.	R = $C_6H_4CH_3$ (*o*)	Acetic acid	Do	60	123-24°	$C_{17}H_{15}O_2N$	N : 5.0	5.3
4.	R = C_6H_4Cl (*p*)	Do	Do	70	111-12°	$C_{16}H_{12}O_2NCl$	N : 4.8	4.7
5.	R = $C_6H_4OCH_3$ (*p*)	Alcohol	Do	68	106°	$C_{17}H_{15}O_3N$	N : 5.2	5.0
			B. 2-Phenylcoumarones (II)					
1.	R = $C_6H_4CH_3$ (*p*)	Alcohol	Colorless plates	85	127-28°	$C_{16}H_{12}O$	C : 86.0 H : 5.5	86.5; 5.8
2.	R = $C_6H_4CH_3$ (*m*)	Do	Colorless prisms	75	78-80°	$C_{15}H_{12}O$	C : 86.0 H : 5.7	86.5; 5.8
3.	R = $C_6H_4CH_3$ (*o*)	Methanol	Do	15*	98°	$C_{15}H_{12}O$	C : 86.1 H : 6.0	86.5; 5.8
4.	R = C_6H_4Cl (*p*)	Acetic acid	Colorless plates	80	149°	$C_{14}H_9OCl$	C : 73.1 H : 4.0	73.5 3.9;
5.	R = C_6H_4OH (*p*)	Do	Colorless prisms	60	192°	$C_{14}H_{10}O_2$	C : 80.3 H : 5.3	80.0; 4.8

* The compound failed to crystallise completely

The authors wish to thank the Ministry of Education, Government of India and the authorities of Patna University for generous grants. Thanks are also due to Principal M. Q. Doja and Professors B. P. Gyani and S. K. Guha for facilities and encouragement.

CHEMICAL LABORATORY,
SCIENCE COLLEGE, PATNA-5.

Received December. 21, 1955.

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

THE HYDROLYTIC CONSTANT AND HEAT OF HYDROLYSIS OF HYDROXYLAMINE HYDROCHLORIDE

By S. S. Muhammad, D. Hanmanth Rao and M. A. Haleem

The hydrolytic constant of hydroxylamine has been determined from conductance and p_H measurements. The heat of hydrolysis derived has been confirmed by solubility and calorimetric experiments.

The hydrolysis of hydroxylamine hydrochloride was first measured by Winkelblech (*Z. physikal. Chem.*, 1901, **36**, 574) and then by Veley (*J. Chem. Soc.*, 1908, **93**, 659). Arneölander (*Z. physikal. Chem.*, 1927, **129**, 1) determined the dissociation constant of hydroxylamine by a colorimetric method. Isikawa and Aoki (*Bull. Inst. Phys. Chem. Res.*, Tokyo, 1940, **19**, 136) and Hagisawa, *ibid.*, 1941, **20**, 251) derived the hydrolytic and dissociation constants from p_H measurements with the glass electrode. But whilst Winkelblech's data implied a K_h value of 6.26×10^{-7} at 25°, Hagisawa's was 10.40×10^{-7}. In view of the discrepancy in the K_h values derived by the above workers, the present study was undertaken, using conductance measurements at different dilutions and temperatures. p_H determinations were made to verify the hydrolytic constant obtained at 30°. Further experiments were carried out to check the heat of hydrolysis from solubility and calorimetric determinations.

Experimental

In the conductance measurements Philips' A.F. oscillator G. M. 2307 was used as the source of A. C. The present experiments were conducted on a frequency of 1 kc./s. A platinum-iridium slide wire of a meter length, a resistance box, a sensitive headphone and Philips' dip type conductivity cell were the other parts of the equipment. Tower's thermostatic unit was used to maintain a constant temperature of the bath. The p_H determinations were carried out with Beckman's p_H-meter, model G.

In the solubility measurements were used tightly stoppered bottles which could be shaken in a bath maintained at the desired temperature. Thermochemical data were obtained with a Cenco vacuum-jacketed calorimeter, using a calibrated Beckmann thermometer.

Hydroxylamine hydrochloride was of B.D.H. Analar quality and gave no test for ammonia. Hydroxylamine was prepared by Hurd and Brownstein's method (*J. Amer. Chem. Soc.*, 1925, **47**, 67). All other chemicals were of Analar grade. Hydroxylamine was estimated iodimetrically as done by Arneölander (*loc. cit.*). Preliminary experiments showed this method as good as the bromate method.

Conductance Data.—After determining the cell constant, the conductivity of hydrochloric acid and of hydroxylamine hydrochloride in aqueous solution and in solution containing added hydroxylamine, were measured. All solutions had the same normality.

According to Ross (Mellor, "Comprehensive Treatise in Inorganic and Theoretical Chemistry", Vol. VIII, p. 284) the conductivity of hydroxylamine salt solutions increases with time due to decomposition of salt on the platinum black electrodes. In order to minimise this, the dip electrodes and salt solutions were kept in the thermostat in separate vessels and the electrodes were dipped in the salt only at the time of taking the resistance reading. The degree of hydrolysis (x) and the hydrolytic constant, K_h, were computed from the usual relations :

$$x = \frac{\text{Conductance of hydrolysed salt—cond. of unhydrolysed salt}}{\text{Conductance of HCl—cond. of unhydrolysed salt}}$$

and $$K_h = \frac{x^2}{(1-x)\,V}$$

where all conductances were measured at the dilution V litres per g. equivalent. The data thus obtained at two temperature are shown in Table I.

TABLE I

Conc.	Hydrolysed salt.	Unhydrolysed salt.	HCl.	$100x$.	$K_h \times 10^7$.
	Conductance at 30°.				
$N/100$	109.74	106.90	451.22	0.83	6.95
$N/1000$	153.24	145.22	462.54	2.53	6.57
$N/5000$	171.19	154.12	464.32	5.50	6.40
$N/10000$	179.40	154 82	465.46	7 91	6.78
					Mean 6.68
	Conductance at 20°.				
$N/100$	108.17	105 82	372.32	0.88	7.81
$N/1000$	150.12	143.73	377.54	2 73	7.65
$N/5000$	165.98	152.44	380 33	5.94	7.50
$N/10000$	174 16	155.25	382.05	8.34	7.59
					Mean 7.64

The p_H measurements were taken at the room temperature (30° ± 0.5°), the relationship used being :

$$PK_h = 2\,p_H - P_c$$

where P terms are negative logarithms of the respective quantities. Table II contains these data.

TABLE II

Conc.	p_H	PK_h	$K_h \times 10^7$.
$N/100$	4 08	6.16	6 92
$N/1000$	4.59	6.18	6.61
$N/5000$	4 94	6 18	6.61
$N/10000$	5.08	6.16	6 92
			Mean 6.77

The values of the hydrolytic constants from conductivity and p_H determinations at 30° are in good agreement. A comparison of the hydrolytic constants at 30° and 20° shows that hydrolysis of hydroxylamine hydrochloride is an exothermic process. Use of Vant Hoff's isochore yields 2.37 k cal. as the heat of hydrolysis.

In the solubility measurements, a saturated solution of hydroxylamine hydrochloride in distilled water and in *N*-HCl was prepared at 15° to 40°, and this was analysed iodimetrically. As hydrolysis is repressed in the presence of HCl, the observations here show the heat of solution of hydroxylamine ; but the data obtained in aqueous solution comprise heat of solution and heat of hydrolysis. Table III records the results of solubility experiments.

TABLE III

Temp. ...	15°	20°	25°	30°	35°	40°
Moles of salt/litre solution in						
(*a*) water ..	18.32	19.49	20 65	21.90	22.99	24.48
(*b*) aq. HCl...	15.85	17.99	20 20	22.98	25.52	28.20

Plots of log solubility against $1/T°$ (absolute) yield the following values of heat changes involved : (*a*) -2.17 ; (*b*) -4.13 k cal. From these the heat of solution -4.13 k cal. and the heat of hydrolysis + 1.96 k cal. may be derived.

In the calorimetric measurements, the water equivalent was obtained from observations on the heat of solution of potassium chloride, taking this to be 4200 cal./mol. (Barieaue and Giaque, *J. Amer. Chem. Soc.*, 1950, **72**, 5676). A thin glass bulb containing a weighed amount of salt was sealed off and dropped into the calorimeter vessel containing a known weight of distilled water or normal hydrochloric acid. The bulb was broken by pressing with the stirrer. Temperature was read on a calibrated Beckmann thermometer. Corrections were made for the heat capacity of thermometer bulb, stirrer and broken tube. The data are recorded in Table IV.

TABLE IV

Water equiv. of calorimeter = 11.80 cals.
Heat capacity of stirrer, thermometer bulb and broken glass = 1.14 cals.

	(*a*) Weight of water taken = 99.5 g.			(*b*) Weight of HCl solution = 101.99 g. Sp. heat of ,, 0.96 cal.		
	Salt taken.	Fall in temp.	Heat change (k cal./mol.)	Salt taken.	Fall in temp.	Heat change (k cal./mol.)
1.	$8.35\times10^{-3}M$	0.13°	−1.750	1. $11.56\times10^{-3}M$	0.41	−3.930
2.	11.59	0.19°	−1.844	2. 9.59	0.35	−4.044
3.	13 03	0.21°	−1.812	3. 7.00	0.25	−3.958
		Mean	−1.80		Mean	−3.98

From Table V, the value of heat of solution is -3.98 k cal. and heat of hydroiysis is + 2.18 k cal.

The heat of solution obtained from solubility and calorimetry are within 1 k cal. of the values given in Rossini's Thermochemistry of Chemical Substances (Reinhold, p. 216) :

Berthelot : -3.35 ; Thomsen : -3.65 ; present authors : -4.13 and -3.98 k cal.

The heat of hydrolysis could not be found in literature ; the values derived in this work from three different methods are in close agreement : conductance + 2.37 ; solubility + 1.96 ; calorimetry + 2.18 k cal.

Besides, the hydrolytic constant, measured conductometrically at 30°, implies a value of 2.202×10^{-8} for the basic dissociation constant of hydroxylamine which agrees with the value obtained spectrophotometrically (reported in the next paper).

Department of Chemistry,
Osmania University,
Hyderabad-Deccan.

Received September 24, 1956.

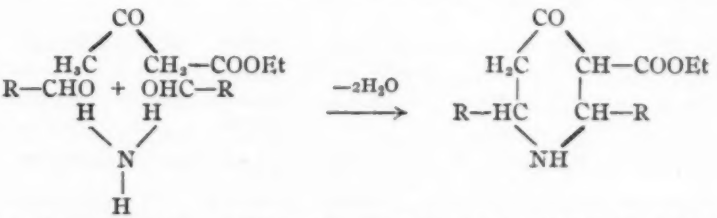
[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

2 : 6-DIARYL-3-ETHOXYCARBONYL-4-PIPERIDONES AND THEIR DERIVATIVES

By P. N. Bhargava and R. P. Singh

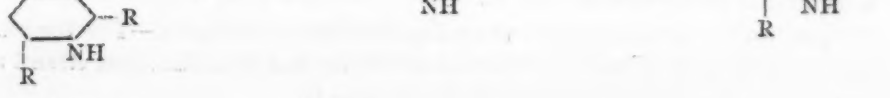
Ten new 2 :6-diaryl-3-ethoxycarbonyl-4-piperidones have been synthesised from ethyl acetoacetate, aromatic aldehydes and ammonia in glacial acetic acid, and their properties as well as characteristic group reactions leading to various derivatives have been studied.

Noller *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 3853) prepared a number of substituted 4-piperidones by condensing ethyl acetoacetate with aromatic aldehydes and ammonium acetate in glacial acetic acid in order to study their analgesic properties.



m-Hydroxybenzaldehyde, vanillin, cinnamaldehyde, salicylaldehyde, *o*-nitrobenzaldehyde, *p*-tolualdehyde, veratraldehyde, *p*-dimethylaminobenzaldehyde, furfural and 2-hydroxy-1-naphthaldehyde have now been employed in the preparation of 2 :6-diaryl-3-ethoxycarbonyl-4-piperidones. The maximum yield of 97% has been obtained in the case of furfural and minimum yield (70%) in the case of 2-hydroxy-1-naphthaldehyde.

The characteristic hydrochlorides of piperidones have been prepared and the carbonyl group condensed with 2 : 4-dinitrophenylhydrazine, yielding 2 : 4-dinitrophenylhydrazones. Condensation with phenylhydrazine and hydroxylamine has yielded substituted pyrazolones and *iso*xazolones respectively which may show a complex pattern of pharmacodynamic behaviour.



Finally the reactive methylene group has been successfully condensed with benzaldehyde. Thus, the structure of the substituted 4-piperidones has been corroborated by preparation of characteristic derivatives and analyses.

EXPERIMENTAL

2:6-Diaryl-3-ethoxycarbonyl-4-piperidones.—A mixture of ethyl acetoacetate (0.25 *M*), aromatic aldehyde (0.5 *M*) and ammonium acetate (0.5 *M*) in glacial acetic acid (35 c.c.) was heated under reflux at different temperatures and time intervals (vide Table I). At the end of the reaction the contents were dissolved in ether and a current of dry hydrogen chloride was passed into it for 15 minutes. The hydrochloride so formed was dissolved in a suitable organic solvent and decomposed with ammonia (conc.) at 0° to precipitate the free base. The data regarding the properties and analyses are recorded in Table I.

TABLE I

No.	Aldehyde condensed.	Refluxed for.	at.	Yield.	Solvent of cryst.	Colour.	M P.	Formula.	% Nitrogen. Found.	Calc.
1.	*m*-Hydroxybenzaldehyde	1 hr.	110°	80%	Benzene-pet. ether	Yellow	167°	$C_{20}H_{21}O_5N$	3 85	3.89
2.	Vanillin	1.5	100°	90	Pet. ether	Yellowish brown	120°	$C_{23}H_{33}O_7N$	3.35	3.40
3.	Cinnamaldehyde	2	100°	86	Do	Brown	112°	$C_{24}H_{25}O_3N$	3.72	3.75
4.	Salicylaldehyde	1.5	160°	80	Benzene-pet. ether	Yellowish brown	176°	$C_{19}H_{21}O_5N$	3.88	3.89
5.	*o*-Nitrobenzaldehyde	1	160°	82	Methanol	Yellow	170°	$C_{29}H_{19}O_7N_3$	10.10	10.15
6.	*p*-Tolualdehyde	4	190°	77	Ethanol-ether	Pale yellow	135°	$C_{22}H_{25}O_3N$	3.86	3.87
7.	Veratraldehyde	2.5	160°	85	*	Brown	110°	$C_{24}H_{29}O_7N$	3.18	3 16
8.	*p*-Dimethylaminobenzaldehyde	2.5	97°	93	Acetone	Yellowish brown	110°	$C_{21}H_{31}O_3N_2$	10.38	10.27
9.	Furfural	3	98°	97	Methanol	Violet	105°	$C_{16}H_{17}O_5N$	4.63	4.65
10.	2-Hydroxy-1-naphthaldehyde	2 5	100°	70	Do	Black	111°	$C_{28}H_{25}O_5N$	3 07	3.08

*Dissolution in phenol and precipitation with alcohol.

2:6-Diaryl-3-ethoxycarbonyl-4-piperidone Hydrochloride.—The piperidone (2 g.) was dissolved in benzene or ether (20 c.c.) and to this HCl (conc., 10 c.c.) was added. The precipitated hydrochloride was filtered and recrystallised from rectified spirit. Relevant data are recorded in Table II.

2.6-Diaryl-3-carbethoxy-4-piperidone-2:4-dinitrophenylhydrazone.—The compound was prepared as usual and after filtration and drying was crystallised from ethanol and ether (1:1). The required data are recorded in Table II.

TABLE II

Aldehydes*.	Diaryl-piperidone hydrochlorides. Yield.	M.P.	Formula.	%Chlorine. Found.	Calc.	Phenylhydrazones. Yield.	M.P.	Formula.	%Nitrogen. Found.	Calc.
No. 1	75%	150°	$C_{29}H_{31}O_5NCl$	8.98	9.06	60%	105°	$C_{35}H_{35}O_5N_5$	12.90	13.08
2.	80	178°	$C_{32}H_{35}O_7NCl$	7.82	7.86	65	89°	$C_{38}H_{39}O_{10}N_5$	11.82	11.76
3.	70	104°	$C_{34}H_{36}O_3NCl$	8.78	8.80	70	95°	$C_{30}H_{29}O_6N_5$	12.66	12 61
4.	65	105°	$C_{29}H_{32}O_5NCl$	9.05	9.07	50	100°	$C_{26}H_{25}O_5N_5$	12.90	13.10
5.	75	165°	$C_{26}H_{30}O_7N_3Cl$	7.84	7.88	68	99°	$C_{36}H_{31}O_{10}N_7$	16.46	16.50
6.	80	148°	$C_{27}H_{26}O_3NCl$	8.98	9.16	70	120°	$C_{25}H_{29}O_6N_5$	13.15	13.20
7.	85	180°	$C_{31}H_{39}O_7NCl$	7.44	7.40	60	108°	$C_{39}H_{33}O_{10}N_5$	11.30	11.23
8.	80	190°	$C_{24}H_{32}O_3N_3Cl$	7.92	7.96	64	109°	$C_{30}H_{35}O_6N_7$	16.68	16.63
9.	68	185°	$C_{16}H_{15}O_5NCl$	10.44	10.46	60	115°	$C_{22}H_{21}O_8N_5$	14.39	14.46
10.	65	205°	$C_{28}H_{26}O_5NCl$	7.26	7.23	50	125°	$C_{31}H_{29}O_8N_5$	10.95	11.02

*The number corresponds to the respective aldehydes as in Table I.

2 : 6 *Diaryl*-3 : 4-*piperidophenylpyrazolone*.—The appropriate piperidone (0.1 *M*) and phenylhydrazine (0.1 *M*) were refluxed in an oil-bath at 125° for 1½ hours. After the reaction, the contents were cooled and treated with alcohol. Most of the tarry matter dissolved leaving behind greyish white solids. These were filtered and crystallised from a suitable solvent. The data regarding properties and analyses are recorded in Table III.

TABLE III

Aldehydes.*	Solvent of cryst.	Yield.	Colour.	M P.	Formula.	%Nitrogen. Found.	Calc.
No. 1	Acetone	80%	Violet	160°	$C_{34}H_{31}O_3N_3$	10.41	10.53
2.	Chloroform	75	Yellow	128°	$C_{36}H_{35}O_5N_3$	9.19	9.15
3.	Acetone	80	Dirty white	131°	$C_{28}H_{25}ON_3$	9.98	10.02
4.	Do	60	Brown	150°	$C_{34}H_{31}O_3N_3$	10.48	10.53
5.	Chloroform	70	Do	146°	$C_{31}H_{35}O_5N_5$	15.31	15.34
6.	Chloroform-methanol	75	Green	152°	$C_{26}H_{25}ON_3$	10.58	10 60
7.	Methanol	76	Yellow	138°	$C_{28}H_{25}O_5N_3$	8 66	8.62
8.	Chloroform	75	Orange	142°	$C_{93}H_{31}ON_5$	15 52	15.45
9	Acetone	85	Brown	166°	$C_{29}H_{17}O_3N_3$	11.89	12.10
10.	Do	65	Black	280°	$C_{32}H_{45}O_3N_3$	8.39	8.41

*The number corresponds to the respective aldehydes shown in Table I.

2: 6-*Diaryl*-3: 4-*piperido*-isoxazolone.—A mixture of the piperidone (0.2 *M*), hydroxylamine hydrochloride (0.2 *M*), sodium acetate (0.3 *M*) and absolute alcohol (15 c.c.) was refluxed on a water-bath for 2½ hours. At the end of the reaction, the contents were poured into ice-cold water (100 c.c.) and stirred well. The precipitate was filtered and crystallised from a suitable solvent. Relevant data are recorded in Table IV.

TABLE IV

Aldehydes.	Solvent of cryst.	Yield.	Colour.	M.P.	Formula.	%Nitrogen. Found.	Calc
No. 1.	Methanol	75%	Yellow	167°	$C_{18}H_{16}O_4N_2$	8.60	8.65
2.	Do	70	Green	150°	$C_{20}H_{20}O_6N_2$	7.32	7.29
3.	Acetone	75	Yellow	168°	$C_{22}H_{20}O_2N_2$	7.95	8.11
4.	Methanol	75	Brown	170°	$C_{18}H_{16}O_4N_2$	8.58	8.65
5.	Do	70	Yellow	190°	$C_{18}H_{14}O_8N_4$	14.58	14.65
6.	Do	65	Do	185°	$C_{26}H_{20}O_2N_2$	8.62	8.65
7.	Do	70	Do	200°	$C_{22}H_{21}O_6N_3$	6.82	6.79
8.	Acetone	75	Do	210°	$C_{22}H_{26}O_2N_4$	14.88	14.81
9.	Methanol	78	Violet	250°	$C_{14}H_{12}O_4N_2$	10.33	10.29
10.	Do	75	Do	198°	$C_{26}H_{26}O_4N_2$	6.58	6.60

2: 6 *Diaryl-3-carbethoxy-5-benzylidene-4-piperidone.*—The piperidone (0.1 *M*) was treated with benzaldehyde (0.1 *M*) and warmed on a water-bath for 10 minutes. On cooling, the product separated and crystallised from chloroform or acetone. The data are recorded in Table V.

TABLE V

Aldehydes.	Yield.	Colour.	M.P.	Formula.	%Nitrogen. Found.	Calc.
No. 1.	50%	Dirty white	140°	$C_{27}H_{25}O_5N$	3.15	3.20
2.	55	Do	130°	$C_{29}H_{29}O_7N$	2.82	2.78
3.	54	Brown	125°	$C_{31}H_{29}O_3N$	2.89	3.02
4.	60	Do	110°	$C_{27}H_{25}O_5N$	3.19	3.16
5.	64	Orange	135°	$C_{27}H_{23}O_7N_3$	8.39	8.38
6.	68	Colorless	128°	$C_{29}H_{29}O_3N$	3.08	3.18
7.	60	Do	150°	$C_{31}H_{33}O_7N$	2.66	2.63
8.	55	Do	155°	$C_{31}O_{25}O_3N_3$	8.48	8.45
9.	50	Brown	138°	$C_{23}H_{21}O_5N$	3.54	3.57
10.	45	Do	146°	$C_{35}H_{29}O_5N$	2.55	2.58

Sincere thanks of the authors are due to the authorities of the Banaras Hindu University for providing necessary facilities.

ORGANIC CHEMICAL LABORATORY,
COLLEGE OF SCIENCE, BANARAS HINDU UNIVERSITY,
BANARAS, U. P.

Received August 8, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

ON SOME FEATURES OF THE TITRATION CURVES OF CARBONIC ACID AND PHOSPHORIC ACID WITH BARYTA

By R. P. Mitra and Hakam Singh

Some hitherto unpublished features of potentiometric and conductometric titration curves of carbonic acid and (ortho) phosphoric acid with baryta have been presented and their significance, in the light of the Mass Action principle and the Phase Rule, pointed out. During the titration of carbonic acid, precipitation of $BaCO_3$ starts from a point where the conductometric titration curve shows a sharp maximum. Precipitation of the carbonate causes an overlapping of the two stages of dissociation and neutralisation of carbonic acid, and only the total quantity of H_2CO_3 is indicated by the titration curve. In the case of phosphoric acid, however, three stages of neutralisation, each culminating in a marked inflexion or break in the titration curve, are clearly indicated for additions of baryta corresponding to the first, the second and the third equivalent of the acid. The monohydrogen phosphate starts getting precipitated when exactly one equivalent of the base has been added. Between the second and the third equivalent of the added base, the p_H and the conductivity remain practically constant. It has been shown that this follows from the Phase Rule remembering that, during the addition of the third equivalent, two solid phases, viz., those of the monohydrogen phosphate and the normal phosphate, coexist.

Carbonic acid and phosphoric acid furnish, as is well known, insoluble barium salts. In potentiometric and conductometric titrations of the acids with baryta, these salts will be precipitated when their solubility products are exceeded. Attention has been drawn below to a number of features of the titration curves of the acids with baryta which follow as a direct consequence of the precipitation of the barium salts. No reference to these features could be found in any published work.

Experimental

Saturated solutions of carbon dioxide were prepared by passing purified carbon dioxide through double distilled water, kept in a constant-temperature bath. The (ortho) phosphoric acid used was "Riedel de Haen A.-G." extra pure quality. The saturated solution of barium hydroxide, used for the titrations, was prepared and kept in CO_2-free atmosphere throughout.

For the potentiometric and conductometric titrations, a fixed volume of the acid solution was taken in each of several pyrex glass bottles to which were then added increasing amounts of the standard alkali solution. After thorough mixing, the bottles were kept, carefully stoppered and sealed (paraffin wax), at a constant temperature in a CO_2-free atmosphere for 24 hours. The p_H and specific conductivity of the contents of different bottles were then determined and titration curves constructed

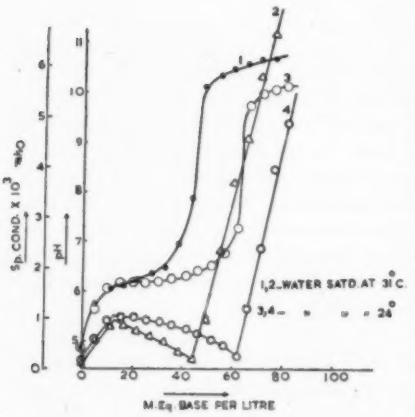
by plotting them against additions of the base. The p_H was measured with a Beckman p_H-meter (model H-2) and Beckman glass electrodes. For the measurements of the conductivity, a Leeds and Northrup Pt-Ir drum-type bridge, a Muirhead audiofrequency oscillator as the source of alternating current, and Muirhead precision resistances as the known arm of the Wheatstone bridge were used.

Discussion

Fig. 1 shows the potentiometric and conductometric titration curves of water, saturated with carbon dioxide at 24° and 31°.

Each conductometric curve (Fig. 1) shows an initially rising portion and then after passing through a sharp maximum, the curve descends to a pronounced minimum, followed finally by a steeply rising straight portion.

Fig. 1



The initial rise in conductivity is evidently due to the formation of barium bicarbonate, $Ba(HCO_3)_2$. The latter dissociates completely giving Ba^{2+} and HCO_3^- ions. At the sharp maximum enough HCO_3^- ions are formed to furnish, by dissociation, an amount of CO_3^{2-} ions, which at the Ba^{2+}-ion concentration obtaining at the sharp maximum, is just sufficient for the solubility product of $BaCO_3$ being reached, as the following calculations will show :

At the sharp maximum, $[Ba^{2+}] = [HCO_3^-] = 1.2 \times 10^{-2}$ g. ions/litre ... (1)

In view of the small value (3×10^{-7}) of the first dissociation constant (K_1) of carbonic acid, the latter affords, by dissociation, only a negligible amount of HCO_3^- ions, and hence, equation (1) gives, to a very fair degree of approximation, the total quantity of HCO_3^- ions in the system at the stage corresponding to the sharp maximum in the conductometric curve.

The concentration of CO_3^{2-} ions at this stage is given by the equation :

$$K_2 = 6 \times 10^{-11} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{[CO_3^{2-}]^2}{1.2 \times 10^{-2}} \quad \ldots \quad (2)$$

where K_2 is the second dissociation constant of carbonic acid.

From (2), $[CO_3^{2-}]$ at the sharp maximum $= 8.48 \times 10^{-7}$ ... ... (3),

and from (1) and (3), the ionic product, $[Ba^{2+}]\,[CO_3^{2-}]$, at the maximum $= 1.01 \times 10^{-8}$, which is equal to or just exceeds the solubility product of $BaCO_3$. Precipitation of $BaCO_3$ should therefore start at the conductometric maximum. This has actually been found to be the case.

As the precipitation of $BaCO_3$ and neutralisation of carbonic acid continue beyond the conductometric maximum, the total ionic concentration of the system

goes on decreasing till the minimum in the conductometric curve is reached, when both the neutralisation and precipitation reactions are completed. The sharp rise in conductivity beyond the conductivity minimum is evidently due to an increasing accumulation of free $Ba(OH)_2$ in the system.

The amounts of CO_2 at the minima of the two conductometric titration curves are 3.25×10^{-2} and 2.45×10^{-2} moles per litre. The pronounced inflexions in the two p_H-titration curves also give the same amounts of CO_2. Hodgeman (Handbook of Chemistry & Physics", 1935, Vol. **20**, p. 890) reports 3.3×10^{-2} and 2.6×10^{-2} moles of CO_2 per litre of water, saturated with the gas at 24° and 31° respectively. Agreement between the two sets of values is fairly satisfactory.

Precipitation of $BaCO_3$ at and beyond the conductometric maximum has a profound influence on the p_H-titration curve also. In the titration of H_2CO_3 with NaOH or KOH, neutralisation of H^+ ions, produced by the dissociation of H_2CO_3 into H^+ and HCO_3^- and of HCO_3^- into H^+ and CO_3^{2-} takes place in two distinct steps, and the titration curve shows two regions of buffering and two inflexions (Britton, "Hydrogen Ions", Chapman & Hall, 1942, Part II, p. 172). However, as will be seen from Fig. 1, the titration curve with $Ba(OH)_2$ shows only one region of buffering and one inflexion. The two stages of dissociation, represented by the equations, $H_2CO_3 = HCO_3^- + H^+$; and $HCO_3^- = CO_3^{2-} + H^+$, merge, and the neutralisation of H^+ ions produced in the two stages proceeds as a continuous process, culminating in the one and only inflexion in the p_H-titration curve. The cause of this merging is to be sought in the precipitation of $BaCO_3$ beyond the conductometric maximum and up to the conductometric minimum. Within this range, the HCO_3^- ions, formed as $Ba(HCO_3)_2$ following each successive addition of $Ba(OH)_2$, dissociates to provide CO_3^{2-} ions. However, since the solution is already saturated with $BaCO_3$, these CO_3^{2-} ions are immediately thrown down as $BaCO_3$, and this process continues till the entire amount of HCO_3^- ions formed on the addition of $Ba(OH)_2$ dissociates, producing (*i*) H^+ ions which are neutralised by the OH^- ions of the base, and (*ii*) CO_3^{2-} ions, which are precipitated as $BaCO_3$. On the whole, therefore, the demands made by the precipitation process are such that the two stages of dissociation,

$$H_2CO_3 = HCO_3^- + H^+ \text{ and } HCO_3^- = CO_3^{2-} + H^+,$$

overlap, and neutralisation of both the H^+ ions proceeds as one continuous process.

Demands of a somewhat different nature on the dissociation and neutralisation of phosphoric acid are made by the precipitation of its insoluble barium salts. This will be seen on a reference to Figs. 2 and 3. Fig. 2 shows the potentiometric and conductometric curves (Nos. 3 and 4) of a 0.02 *M* solution of H_3PO_4 with 0.295 *M*-$Ba(OH)_2$. Titration curves (Nos. 1 and 2) of this acid with KOH are also given in the same figure for comparison. Fig. 3 shows the titration curves of a concentrated solution (0.093 *M*) of H_3PO_4 with $Ba(OH)_2$ depicting the final stages of the neutralisation of this acid with the base.

FIG. 2

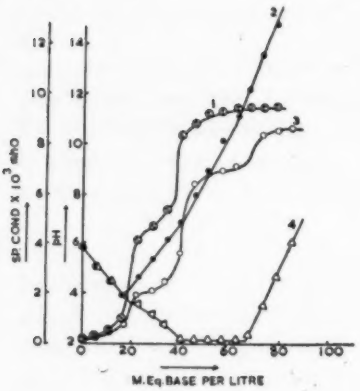
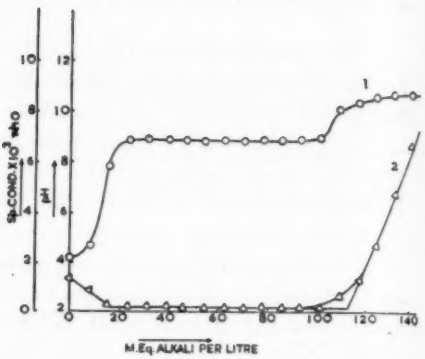


FIG. 3



The p_H-titration curve (No. 1) with KOH, shown in Fig. 2, exhibits, as expected, only two inflexions, indicating a stepwise neutralisation of H^+ ions produced in the first two stages of dissociation :

$$H_3PO_4 = H^+ + H_2PO_4^- \text{ and } H_2PO_4^- = H^+ + HPO_4^{2-}.$$

The end-point of the third stage of neutralisation is, as is well known, masked by hydrolytic effects. The p_H-titration curve (No. 3) with $Ba(OH)_2$, shown in Fig. 2, however, clearly brings out the three steps in the neutralisation of the acid. The curve shows three inflexions, and the acidities at these inflexions are as 1 : 2 : 3, as should be the case. The conductometric titration curve (No. 4) with baryta also shows three distinct changes of curvature corresponding to the three inflexions in the p_H-titration curve.

Beyond the first inflexion in the p_H-titration curve, the monohydrogen phosphate, $BaHPO_4$, is formed and we have found that this salt is precipitated when exactly 1.0 equivalent of $Ba(OH)_2$ is added, that is, immediately following the first inflexion in the titration curve. Britton ("Hydrogen Ions", Chapman and Hall, 1942, Part II, p. 118) found that 1.62 equivalents were required to start precipitation. However, as Britton himself reports, the E. M. F's recorded by him during the course of the titration "were not true equilibrium values" but were those measured immediately after each addition of the base. Actually, Britton found that though the precipitation of $BaHPO_4$ started at p_H 6.88 after 1.62 equivalents of base had been added, on standing overnight, further precipitation occurred and the p_H of the solution fell to 6.07. Evidently, the titration curve of phosphoric acid with baryta, reported by Britton (*ibid.*, Part I, p. 193), does not depict equilibrium conditions as sufficient time was not allowed for the processes of neutralisation and precipitation to complete themselves. In our titrations, sufficient time was allowed for the equilibrium to be established and with this precaution, the $BaHPO_4$ was precipitated when exactly 1.0 equivalent of the base had been added, as already mentioned.

Our baryta-titration curve is different from that of Britton in another even more important respect. Britton's curve shows only two inflexions as against the 'three' inflexions observed by us. As noted by Britton himself, the second inflexion in his curve, "occurred during the addition of the third equivalent" of the base, from which he concluded that the precipitate which came down at this stage was a "mixture of di- and tribarium phosphates". Here again, we believe that Britton's failure to record a third inflexion and also the fact that his titration curve showed its second (and final) inflexion much before the third equivalent had been added, are really to be attributed to an incomplete reaction between the reactants as the time allowed for the interaction was not quite sufficient for this purpose. If sufficient time had been allowed for the reactions to complete themselves, a second and a third inflexion would have been observed corresponding to the addition of a second and a third equivalent of the base, as our experience shows.

In our titration, the formation and precipitation of $BaHPO_4$ are complete at the second inflexion. The reaction with the base beyond the second inflexion is therefore really one between increasing amounts of the added base and a saturated solution of $BaHPO_4$ which also contains an excess of solid $BaHPO_4$. The product of this reaction, $Ba_3(PO_4)_2$, is again another insoluble salt which separates out as a second solid phase as the reaction proceeds.

A striking feature of the reaction between the second and the third inflexion is the fact that both the p_H and the conductivity of the system remain practically constant during this stage. This will be particularly seen from the titration curves in Fig. 3, depicting the course of the third stage of the reaction between a 0.093 *M* solution of H_3PO_4 and baryta. Both the p_H- and conductivity-curves appear as practically straight horizontal portions during this stage.

Actually, the above features are demanded by and are in harmony with the Phase Rule. As already pointed out, at any stage of the reaction between the second and the third inflexion, the system contains two solid phases, viz., $BaHPO_4$ and $Ba_3(PO_4)_2$. These two solid phases and liquid water as well as water vapour, making in all four phases, are in equilibrium. There are three components which may be any three of $BaHPO_4$, $Ba_3(PO_4)_2$, H_2O and $Ba(OH)_2$. The system is therefore univariant. If now the temperature is maintained constant, as was actually done during the titration, the system loses its only degree of freedom, that is, becomes non-variant, and this is why the composition of the system remains constant during the reaction, as illustrated by the constancy of both the p_H and the conductivity.

Thanks of one of the authors (H.S.) are due to the Ministry of Education, Government of India, for the award of a Senior Research Scholarship during the tenure of which this work was done.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DELHI,
DELHI-8.

Received August 28, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

POTENTIOMETRIC DETERMINATION OF TRIPOSITIVE ANTIMONY WITH ALKALINE HYPOCHLORITE

By (Miss) Safura Khatun and M. H. Khundkar

A new method has been developed for potentiometric determination of tripositive antimony with alkaline sodium hypochlorite. The titration is satisfactory at elevated temperatures (above 75°) and in presence of a minimum of 3-5% NaOH. Under these conditions, antimony can be determined within an error of less than 1%.

The most commonly used volumetric method for the determination of tripositive antimony is titration with $KBrO_3$:

$$KBrO_3 + 3\ SbCl_3 + 6HCl = 3\ SbCl_5 + KBr + 3\ H_2O.$$

In the conventional method using methyl orange, the end-reaction is slow and often leads to over-titration, particularly if HCl concentration is not sufficient. Belcher (*Anal. Chim. Acta*, 1949, **3**, 578 ; 1951, **5**, 30) found that naphthoflavone and quinoline-yellow behaved reversibly and could be used satisfactorily in the above titration.

In the iodine oxidation,

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI,$$

the usually acid solutions are to be neutralised with $NaHCO_3$ and titration completed immediately after this.

The titration of tripositive antimony with KIO_3 up to the iodine monochloride end-point,

$$KIO_3 + 2\ SbCl_3 + 6\ HCl = 2\ SbCl_5 + KCl + ICl + 3\ H_2O$$

was thoroughly studied by Hammock *et al.* (*Anal. Chem.*, 1948, **20**, 1048) who found the titration possible only within a narrow limit of acidity (2.5 – 3.5 *N*).

In course of an investigation on the dissolution of antimony ore (stibnite) trivalent antimony was observed to be quantitatively oxidised with alkaline hypochlorite solution. A potentiometric method has now been developed for satisfactory and quick determination of trivalent antimony.

$$Sb_2O_3 + 2\ NaOCl = Sb_2O_5 + 2\ NaCl$$

The present paper deals with the effects of different variables.

Experimental

N/10 alkaline sodium hypochlorite was prepared by passing chlorine into 0.4*N*-NaOH (~), boiled and finally standardised according to Kitchener *et al.* (*Analyst*, 1951, **76**, 509).

No suitable indicator could be found for volumetric titration without use of the potentiometer. Use of a known excess of alkali hypochlorite to the alkaline solution

of Sb_2O_3 and then back-titrating the excess hypochlorite also led to erroneous results, for the obvious reason that Sb^{5+} also took part in the reaction.

Finally the potentiometric method was used. A definite amount of Sb_2O_3 was dissolved in a definite volume (100 c.c.) of 5% NaOH by warming and made to a final volume of 150 c.c. During the titration, the solution was maintained between 80° and 90° and hypochlorite added from a burette. The change in potential was measured in the usual way with a platinum electrode by coupling with a standard calomel e ectrode. The inflection near the end-point was very clear, being (approx.) 0.05 to 0.10 volt per 0.1 c.c. Experiments were also done with $SbCl_3$.

Discussion

Effect of Temperature.—As the ease of solubility of Sb_2O_3 in alkali depends on temperature, possibility of satisfactory titration may be hampered by change (lowering) of temperature. Results of different experiments are shown in Table I.

Table I

Temp.	Antimony taken.	Antimony found.	Diff.
28°	0.0376 g.	—	—
50-55°	0.0376	0.0383 g.	+ 0.7 mg.
50-55°	0.0376	0.0382	+ 0.6
70-75°	0.0376	0.0375	− 0.1
80-85°	0.0376	0.0378	+ 0.2

Erroneously high results are obtained at room temperature. Moreover, the potentiometric curve did not show any clear inflexion point, but changed in a more or less uniform fashion. At 50-55°, a sharp end-point was obtained from potentiometric reading, but the results were slightly higher. Satisfactory results were obtained at 70-75° or higher temperature. But as the end-point is more prominent at 80°-85°, this temperature is recommended for further work.

Effect of Alkali Concentration.—The solubility of Sb_2O_3 in water even at 85° is low. When the Sb_2O_3 was taken in water (instead of alkali) a clear solution was not obtained, and potential change did not show any distinct inflexion point.

Thus, for satisfactory titration, alkali contained in hypochlorite was insufficient and in a series of experiments the Sb_2O_3 was dissolved originally in NaOH having different concentrations.

Table II

Temp. = 85° ± 2.5°.

Conc. of NaOH used for dissolving Sb_2O_3.	Antimony taken.	Antimony found	Diff.
1.0 %	0.0376 g.	0.0430 g.	+ 5.4 mg.
3.0	0.0376	0.0377	+ 0.1
5.0	0.0376	0.0378	+ 0.2
8.0	0.0376	0.0375	− 0.1

Even with an alkali concentration of 1%, except probably for some initial disturbances, the titration was satisfactory, showing a distinct end-point. The result was somewhat higher. With 3-5 % alkali solution, the results were satisfactory, and there was no error in the result even when the alkali concentration was 8%. In fact, in the last experiment, the E. M. F./volume curve was most satisfactory.

Determination of Antimony in varying amounts of Sb_2O_3 *and* $SbCl_3$ —After setting the optimum conditions for best titrations, varying proportions of Sb_2O_3 were determined in separate experiments. A comparison has been made of the present method with the $KBrO_3$ determination (Table III).

TABLE III

Alkali concentration = 5%. Temp. = 85-90°.

Sb taken.	Sb found by potentiometric method (NaOCl)	Diff.	Sb found by $KBrO_3$ method.	Diff.
0.0134 g.	0.0135 g.	+ 0.1 mg.	0.0137 g.	+ 0.3 mg.
0.0251	0.0250	− 0.1	0 0253	+ 0.2
0.0376	0.0378	+ 0.2	0.0380	+ 0.4
0.0501	0 0502	+ 0.1	0.0502	+ 0 1
0.0668	0.0666	− 0.2	0.0672	+ 0.4

It will be seen that within the range of our experiments, results of potentiometric titration are quite satisfactory and within 1% error. It may be considered superior to $KBrO_3$ titration, in which case there is always a positive error (over-titration), and difference relatively wide. This error in $KBrO_3$ is well known.

TABLE IV

Comparison of results of the titration of $SbCl_3$ *by diff. methods.*

Sb found by							
Potentiometric (NaOCl)	...	0.0434	0.0492	0 0578	c.0654	0.0867	0.1054
$KBrO_3$	...	0.0438	0 0496	0 0582	0.0658	0.0868	0.1063
Iodine	...	0.0431	0.0491	0.0577	0.0650	0 0863	0.1049

In the case of antimony trichloride (Table IV), stock solutions were made by weighing (not accurately, as the material is hygroscopic) different amounts. Aliquot portions from each sample were titrated against NaOCl, and also with $KBrO_3$ and standard iodine solution.

For hypochlorite titration, the acid solution was neutralised with 5% NaOH, when at first a precipitate was formed which ultimately dissolved in excess alkali on warming. The rest of the titration was as usually found with Sb_2O_3.

DEPARTMENT OF CHEMISTRY,
DACCA UNIVERSITY, DACCA,
EAST PAKISTAN.

Received July 11, 1956.

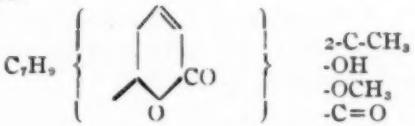
[Jour. Indian Chem. Soc., Vol. 34, No.2, 1957]

THE CONSTITUTION OF SWIETENINE, THE NON-BITTER PRINCIPLE OF THE SEEDS OF *SWIETENIA MACROPHYLLA* KING. PART II

By Tarakeswar Chakrabartty and Asima Chatterjee (nee Mookerjee)

Swietenine, $C_{18}H_{24}O_5$, the non-bitter lactonic principle of *Swietenia macrophylla*, upon dehydrogenation with selenium at 300° in a sealed tube produces a hydrocarbon, swieten, $C_{16}H_{20}$ It has been characterised as a polyalkylnaphthalene from its U. V. spectrum and other pertinent physical and chemical data. This observation, coupled with chemical and spectral evidences, indicates a hydronaphthalene lactone structure for swietenine.

Swietenine, the non-bitter, lactonic principle of *Swietenia macrophylla* King (N. O. *Meliaceae*) was reported earlier to have the partial structure (I) by the present authors (this *Journal*, 1955, **32**, 179).

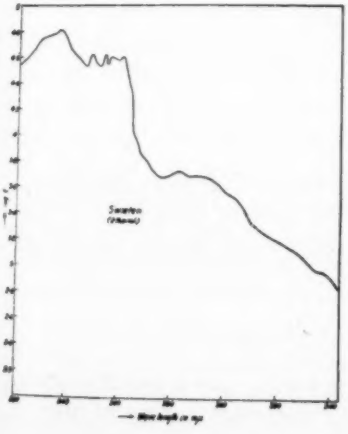


(I)

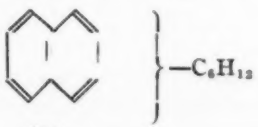
Further elucidation of its constitution has been possible from a study of the nature of its selenium dehydrogenation products. A discussion on this subject and relevant data are presented here. Dehydrogenation experiments were carried out with swietenine both in sealed and open tubes.

With black selenium at 300° in a sealed tube, swietenine smoothly decomposed giving rise to a mixture of several compounds from which a liquid hydrocarbon (b. p. 129°/0.03 mm) was obtained as the principal constituent. This compound has been designated as swieten, $C_{16}H_{20}$, although the possibility of its having $C_{17}H_{22}$ formula cannot be excluded simply from C-H analyses. This point can only be clarified by the synthesis of swieten, which is under way. The hydrocarbon was rendered pure and homogeneous by repeated chromatography over Brockmann alumina (vide Experimental). It exhibits a bluish violet fluorescence in solution and readily forms an orange crystalline trinitrobenzolate which analyses for $C_{16}H_{20}.C_6H_3(NO_2)_3$. Swieten carries two methyl groups. Its ultraviolet spectrum (Fig. 1) (λ_{max} at 238 mμ, log ϵ 4.81 and at 283 mμ, log ϵ 3.72) resembles closely that of alkylnaphthalenes and exhibits a bathochromic shift characteristics of polyalkylated naphthalene derivatives (Braude, *Ann. Reports*, 1945, **42**, 105). From U. V. spectrum and extinction values

FIG. 1

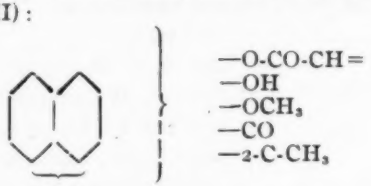


swieten is thus proved to be a polyalkylated naphthalene. The possibility of its being a phenanthrene, anthracene or phenalan derivative has also been considered. The first two appear to be unlikely from a consideration of (*a*) their ultraviolet spectra (Braude, *loc. cit* ; Morton and De Gouveia, *J. Chem. Soc.*, 1934, 927 ; Askew, *ibid.*, 1935, 509 ; Cocker and Hayes, *ibid.*, 1951, 844 ; Mosby, *J. Amer. Chem. Soc.*, 1953, **76**, 3848 ; Heilbronner, Fröklicher and Plattner, *Helv. Chim. Acta*, 1949, **32**, 2479), (*b*) high percentage of hydrogen in swieten, and (*c*) ready oxidation of its -C.Me functions which is not to be expected if the methyl groups are directly attached to the anthracene and phenanthrene nucleus. A tetrahydrophenanthrene or tetrahydroanthracene expression for swieten (methyl groups in reduced rings) would not be unlikely. But they are readily transformed into the corresponding aromatic systems at 300° in presence of selenium, as experienced from model experiments. The phenalan constitution of swieten is also untenable although its U. V. spectrum (Buchi and Pappas, *J. Amer. Chem. Soc.*, 1954, **76**, 2963) is similar to that of naphthalene and swieten. The latter, unlike phenalan, fails to undergo (*a*) catalytic hydrogenation and (*b*) does not form keto-dicarboxylic acid on oxidation with potassium ferricyanide (Buchi and Pappas, *loc. cit.*). From a consideration of all available evidence, swieten could best be represented by polyalkylnaphthalene structure (II).



(II)

Now, swietenine, from which swieten (II) is derived, is not an aromatic compound. Therefore, the naphthalene moiety in (II) must have been formed from the corresponding hydronaphthalene system occurring in swietenine, and the most probable constitution of this substance thus appears as (III) :



(III)

The positions of the lactone ring and other functional groups are yet to be ascertained and further work in this line is in progress. But from the present knowledge of the chemistry of swietenine, it can be said that the lactone ring remains directly fused with the hydronaphthalene nucleus.

EXPERIMENTAL

Selenium Dehydrogenation of Swietenine in a sealed tube.—An intimate mixture of swietenine (1.0 g.) and black pulverised selenium (1.0 g.) was heated in a sealed tube at 300° for 4 hours, and then at 310°-320° for 5 hours. After cooling, the tube was broken

and the brown mass was extracted with ether which was evaporated off. The gummy residue was taken up with petroleum ether (b. p. 40°-60°) and filtered through a column of Brockmann alumina. The filtrate on evaporation left a brown mass which on high vacuum sublimation at 120-50°/0.03 mm gave an orange coloured viscous oil (0.80 g.). This was dissolved in 30 c.c. of petroleum ether and the clear solution, thus obtained, was column-chromatographed over alumina (18 cm × 1 cm), using the same solvent as eluent. The eluate was collected in six fractions of 5 c.c. each. The results are recorded in Table I.

TABLE I

Fractions.	Product on evaporation.	Yield.
1	Brown liquid	16 mg.
2	Orange, viscous liquid exhibiting blue flourescence	29
3	Do	20
4	Do	9
5	Nil	...
6	Nil	...

Alcoholic solution of each of the residues from fractions 2, 3 and 4, on treatment with alcoholic trinitrobenzene, yielded identical silky orange crystalline trinitrobenzolate, m. p. 152.5-53° which showed no depression in their mixed melting points. [Found (in a sample dried in *vacuo* over P_2O_5 for 4 hours at 80°): C, 63.35 ; H, 5,61 ; N, 9.34 ; -C.Me, 7.16. $C_{16}H_{20}.C_6H_3(NO_2)_3$ requires C, 62.12 ; H, 5.41 ; N, 9.88 ; 2C.Me, 7.06%).

Regeneration of Swieten.—The trinitrobenzolate (0.1 g.) was decomposed chromatographically over activated alumina (50 mg.) using petroleum ether as the eluent. The pure and homogeneous swieten, isolated thereby, distilled at 120°/0.03 mm, yield 40 mg. It formed crystalline trinitrobenzolate, m. p. 152.5-153° which did not show depression when mixed with the trinitrobenzolates obtained before. The ultraviolet absorption spectrum of swieten (Fig. 1) shows the maximum at 238, 249, 254 and 283mμ, corresponding log ε values being 4.81, 4.62, 4.62 and 3.72 respectively. It failed to take up hydrogen when its alcoholic solution was subjected to catalytic hydrogenation in presence of Adams' catalyst. (Found in a dry sample: C, 89.92 ; H, 9.42 ; C.Me, 13.01. $C_{16}H_{20}$ requires C, 90.57 ; H, 9.43 ; 2 C.Me, 14.15%).

Fraction (1) (Table I) furnished a brown oily gum. It showed no tendency to crystallise but could be coupled with diazobenzene chloride to a red solid in alkaline solution. With alcoholic ferric chloride it developed a green coloration. A red intractable gummy product was obtained when this phenolic portion was treated with an alcoholic solution of trinitrobenzene.

Selenium Dehydrogenation of Swietenine in an open tube.—An intimate mixture of swietenine (0.5 g.) and selenium powder (0.5 g.) was heated in a metal-bath at 350° for 30 minutes. The dark brown mass was allowed to cool and the test tube with its contents was crushed with sea-sand and soxhletted with benzene for 16 hours. The

brown benzene extract having a green fluorescence was filtered and the filtrate on evaporation of the solvent left a brown gummy residue which on high vacuum distillation at 110-120°/0.01 mm, yielded an orange coloured viscous oil (30 mg.). It did neither crystallise nor produced crystalline picrate with alcoholic picric acid.

The authors thank Mr. W. Manser, Eidg. Technische Hochschule, Zürich, Switzerland and Mrs. Chabi Dutta, Department of Pure Chemistry, University College of Science, for microanalyses. They further acknowledge their deep appreciation to the Government of West Bengal for financial assistance.

DEPARTMENT OF CHEMISTRY,
KRISHNAGAR COLLEGE
AND
UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

Received July 31, 1956.

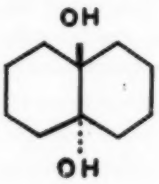
[Jour. Indian Chem. Soc., Vol. 34, No.2, 1957]

ACTION OF PREVOST'S REAGENT ON $\Delta^{9:10}$-OCTALIN

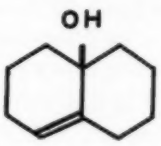
By Sukh Dev

The action of silver benzoate-iodine complex on $\Delta^{9:10}$-octalin has yielded 9-oxy-Δ^{4}-octalin instead of the expected 9:10-glycol.

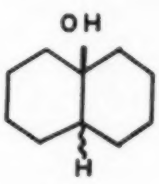
The silver benzoate-iodine complex is a useful reagent for the hydroxylation of an ethylenic linkage (Prevost *et al.*, *Compt. rend.*, 1933, **196**, 1129 ; 1933, **197**, 1661 ; 1934, **198**, 2264 ; 1937, **204**, 989 ; Hershberg, *Helv. Chim. Acta*, 1934, **17**, 351 ; Niemann and Wagner, *J. Org. Chem.*, 1942, **7**, 227) ; the addition of the two hydroxyls is stereospecific and always *trans* (Wittcoff and Miller, *J. Amer. Chem. Soc.*, 1947, **69**, 3138 ; Sletzinger and Dawson, *J. Org. Chem.*, 1949, **14** 849). In connection with the preparation of decalin-9:10-diol (Sukh Dev, this *Journal*, 1954, **31**, 1) the action of Prevost's reagent on $\Delta^{9:10}$-octalin was studied. The chief product surprisingly was found to be an olefinic alcohol ; the expected *trans*-glycol (I) could not be isolated.



(I)



(II)



(III)

This product has been assigned the structure (II) on the basis of the following evidence: The elemental analysis indicates the formula $C_{10}H_{16}O$. The compound imparts a yellow colour with tetranitromethane. The substance is fairly labile and during distillation (at 5 mm.) is partially dehydrated to a conjugated diene (*vide infra*) ; this behaviour is consistent with the $\alpha\beta$-unsaturated *tert.*-carbinol system, which is expected to be susceptible to ready dehydration (cf. Sukh Dev, *ibid.*, 1955, **32**, 325). Its infra-red spectrum had bands (relevant) indicated in Table I with the most likely assignments.

TABLE I

	ν (cm.$^{-1}$.)	Assignment.	Reference.
(i)	3340 (S), Broad	O—H stretching; intermolecular hydrogen bonds.	Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen & Co. Ltd., London, 1954, p. 83.
(ii)	1650 (S)	C=C stretching.	Jones & Sandorfy in Weissberger's "Technique of Org. Chem ", Interscience Publishers, New York, 1956, Vol. 4, p. 369.
(iii)	840 (M)	C—H out-of-plane bending vibrations for a substituted olefine.	Jones & Sandorfy, *loc. cit.*, p. 382.

In the C—OH stretching frequency range (1000-1200), several peaks occur, out of which the doublet at 1055 and 1040 is the strongest, and taking into account the known shift (about 60 cm^{-1}) towards the lower frequencies caused by an olefinic linkage when present at the $\beta\gamma$-position to a hydroxyl (Zeiss and Tsutsui, *J. Amer. Chem. Soc.*, 1953, **75**, 897), may possibly be assigned to the C—OH stretching vibrations of the $\alpha\beta$-unsaturated *tert.*-carbinol system. That this olefinic linkage is tri-substituted has further been confirmed by the end-absorption (Table II) in the ultraviolet region (Bladon *et al.*, *J. Chem. Soc.*, 1952, 2737 ; Halsall, *Chem & Ind.*, 1951, 867 ; Dawson *et al.*, *J. Chem. Soc.*, 1953, 590).

TABLE II

End-absorption.

λ.	ε.	ε for a tri-substituted ethylenic linkage (Bladon *et al.*, *loc. cit.*).
210 mμ	4035	1400-4700
215	2480	600-3500
220	1570	250-1800
225	1335	...

All these data are consistent with the structure (II). A final confirmation of the structure (II) by catalytic hydrogenation to the known (III) (Elsevier's Encyclopaedia of Organic Chemistry, Amsterdam, 1950, Vol. 12B, p. 1378) could not be achieved, since the compound resisted hydrogenation over Pd—$CaCO_3$ catalyst in ethanol, and over Adams' catalyst in glacial acetic acid hydrogenolysis occurred as evidenced by no break at the stage of 1 mole hydrogen absorption.

The alcohol (II), as has been stated above, dehydrated partially during distillation to yield a diene which developed an orange-red colour with tetranitromethane and coupled with diazotised *p*-nitroaniline to furnish a red dye. The latter reaction is characteristic of conjugated dienes (Meyer, *Ber.*, 1919, **52**, 1468 ; Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 160 ; Bachman and Hatton, *ibid.*, 1944, **66**, 1513). The same hydrocarbon could be obtained readily by the dehydration of (II) over potassium bisulphate ; the two products were shown to be identical by their ultraviolet spectra. The acid-catalysed dehydration of the alcohol (II) can theoretically lead to four dienes (IV, V, VI and VII). Since the product obtained has λ_{max} at 242 mμ, the thermodynamically stabler structure (IV) is indicated ; the calculated λ_{max}

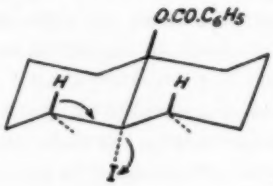
(IV) (244 mμ) (V) (282 mμ) (VI) (234 mμ) (VII) (273 mμ)

values according to Woodward-Fieser rules (Dorfman, *Chem. Rev.*, 1953, **53**, 59) have been indicated below each structure. In confirmation of this structure, the diene on lithium-liquid ammonia-alcohol reduction furnished $\Delta^{9:10}$-octalin. As expected of a hetero-annular diene (Alder, "Newer Methods of Preparative Organic Chemistry", Interscience

Publishers, New York, 1948, p. 383 ; Bergmann and Hirsmann, *J. Org. Chem.*, 1939, **4**, 40), the compound furnishes a very poor yield of the maleic anhydride adduct, which is more likely to be derived from the homo-annular diene (V), produced under the reaction condition of the diene synthesis ; such a behaviour is well recognised (Ruzicka *et al.*, *Helv. Chim. Acta*, 1937, **20**, 1542 ; 1940, **23**, 1346 ; Goodway and West, *J. Chem. Soc.*, 1938, 2028).

Nametkin and Glagoleff (*Ber.*, 1929, **62**, 1570) have described a hexalin (IV and/or V) obtained by the dehydration of decalin-9 : 10-diol with dilute sulphuric acid at 150° ; the physical data obtained for (IV) in the present work rule out this structure for the hexalin of Nametkin and Glagoleff. The 9 : 10-glycol could not be dehydrated by refluxing its benzene solution in the presence of iodine or *p*-toluenesulphonic acid ; with formic acid (87%) at 100° the glycol yielded only a polymerised product.

There is sufficient evidence to show that the first step in the Prevost oxidation is the addition of the pseudo-halogen ($R.CO.O\overset{\Delta^-}{—}\overset{\Delta^+}{Hal}$) to the olefine (Waters in Gilman's "Organic Chemistry : An Advanced Treatise", John Wiley & Co., New York, 1953, Vol. IV, p. 1230) to give a halo-acyloxy derivative (Birckenbach *et al.*, *Ber.*, 1932, **65**, 1339; Bockemuller and Hoffmann, *Annalen*, 1935, **519**, 165 ; Uschakow and Techistow, *Ber.*, 1935, **68**, 824 ; Halperin *el al.*, *J. Org. Chem.*, 1952, **17**, 623). The halogen atom, evidently, then undergoes a nucleophilic displacement by the anion ($R.COO^-$) with retention of configuration (Winstein *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 2784, 2787 ; 1943, **65**, 2096 ; 1946, **68**, 118) to yield the *trans*-glycol derivative (cf. the preparation of *cis*-glycols by a modified Prevost oxidation : Ginsburg, *ibid.*, 1953, **75**, 5747 ; Barkley *et al.*, *ibid.*, 1954, **76**, 5014). In the present investigation the expected intermediate



(VIII)

(VIII) has a tertiary iodo group in the axial conformation, which is coplanar with the axial hydrogen of the neighbouring methylene groups and so E2 takes precedence ; it is well established that tertiary halides are more susceptible to an elimination reaction (Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, p. 434) and that for a concerted bimolecular reaction, the four centres of importance must lie in one plane (Barton, *J. Chem. Soc.*, 1953, 1027). It may be predicted from this result that in a rigid system containing a tetra-substituted ethylenic linkage, the Prevost oxidation would most likely lead to an unsaturated alcohol of the type (II), provided an axial hydrogen would be available for elimination.

EXPERIMENTAL

Melting and boiling points are uncorrected. The ultraviolet spectra were taken in ethanolic solution on a Beckman DU spectrophotometer.

Action of Silver Benzoate-iodine Complex on $\Delta^{9:10}$*-Octalin.*—In a litre flask, fitted with an adapter carrying a dropping funnel, a distillation head topped with a reflux condenser and a slip-seal point for a Hershberg stirrer, was placed a mixture of dry silver benzoate (54.9 g., 0.24 *M*) and anhydrous benzene (250 c.c.), and with stirring benzene (*ca.* 50 c.c.) was distilled off to secure perfect anhydrous conditions. The contents were allowed to cool to room temperature and a solution of iodine (25.5 g., 0.2 g. atom) in benzene (300 c.c.) was let in with stirring. To the yellowish complex, thus obtained, the octalin (13.6 g., 0.1 *M*) in benzene (30 c.c.) was introduced (10 mins.) and the reaction mixture was stirred and refluxed for 18 hours. The precipitated AgI was filtered off and washed with benzene (50 c.c. × 3). From the combined filtrates the solvent was flashed off (column) from a steam-bath under slight suction. The residue crystallised out on cooling and the crystals (a test portion recrystallised from benzene-petrol) were shown to be benzoic acid (m. p. and mixed m. p.). The residue was treated with KOH (20 g.) in ethanol (100 c.c.) containing water (20 c.c.) and refluxed for 2 hours. The product was diluted with water (500 c.c.), extracted with ether (60 c.c. × 4), washed with brine (50 c.c.) and dried (Na_2SO_4). The solvent was removed and the residue fractionated through a Vigreux column (12″) carrying a total condensation type still-head to give fractions: (*i*) b. p. 60-62°/3mm, 3.5 g. (*ii*) b. p. 95-104°/3 mm, 8.5 g. and (*iii*) residue *ca.* 1 g.

Fraction (*i*) was rectified over sodium to furnish a hydrocarbon (3 g.), b. p. 80-84°/12 mm, η_D^{26} 1.5035, which was apparently a mixture of the starting material and the diene (V; *vide infra*), and from its η, was computed to contain about 75% of octalin; the presence of this hydrocarbon was established by the preparation of *trans*-9:10-dibromodecalin (Hückel *et al.*, *Annalen*, 1929, **474**, 134), m. p. 137-58°(pet. ether), which was undepressed on admixture with an authentic sample.

The second fraction was observed to dehydrate on refractionation at 5 mm, and hence, the entire distillate (7.5 g., b. p. 69-107°/5 mm) was refractionated at 2 mm. The fractionation assembly was pretreated with warm aqueous Na_2CO_3 solution for a few hours to destroy any hydrogen ions on the glass surface. Following sub-fractions were thus obtained: (*a*) b. p. 60-61°/2 mm, η_D^{30} 1.5295, yield 3.0 g., this was identified as the diene (V) (*vide infra*). (b) b. p. 100-102°/2 mm, η_D^{30} 1.5140, yield 3.0 g., this product was characterised as 9-*oxy*-Δ^4-*octalin* (II). It is a colorless thick liquid with the characteristic musty decalol odour and an anlaytical sample had η_D^{31} 1.5155, d_4^{31} 1.014, M_D 45.25 (calc. for $C_{10}H_{16}O$: $\overline{\overline{\text{I}}}$: 45.05). (Found: C, 78.43; H, 10.59. $C_{10}H_{16}O$ requires C, 78.94; H, 10.52%). Its infra-red spectrum was measured on a Perkin-Elmer double-beam instrument* on the pure liquid (smear) and had the following bands besides those recorded in Table I: 2900 (S; broad), 2640 (W), 1630 (M), 1440 (S), 1392 (S), 1350 (M), 1320 (S), 1285 (S), 1215 (M), 1180 (S), 1165 (S), 1140 (S), 1110 (M), 1077 (S), 1055 (S), 1040 (S), 1025 (S), 1005 (S), 985 (M), 960 (S), 945 (S), 910 (M), 880 (M).

The original fractionation residue (fraction *iii* above) was examined for the presence of the glycol (I). The residue was sublimed at 100°/35 mm and the sublimate (*ca.* 50 mg., wax) was crystallised from dilute acetone to afford white nodules (*ca.* 5mg.) of m. p. 171-73°, which were not studied further.

* Through the courtesy of Charanjit Rai

$\Delta^{4:8}$-Hexalin (V).—The above-mentioned sub-fraction (*a*) was rectified over sodium to provide a colorless liquid, which was very susceptible to polymerisation, b. p. 81-82°/9 mm, η_D^{30} 1.5295, yield 2.5 g. The central cut had : η_D^{31} 1.5300, d_4^{31} 0.9358, M_D 44.23 (calc. for $C_{10}H_{14}$: $\sqrt{2}$ 43.06 ; $E\Sigma_D$, 0.87) ; λ_{max} 242mμ (ϵ, 13670). (Found : C, 89.63 ; H, 10.33. $C_{10}H_{14}$ requires C, 89.55 ; H, 10.44%).

The olefinic alcohol (II) (500 mg.) was also dehydrated by its rapid (2 mins.) distillation at 7 mm over finely powdered fused $KHSO_4$ (25 mg.) ; the distillate was redistilled over $KHSO_4$ as before and the final material (b. p. 75-79°/7 mm) was rectified over sodium to yield the diene (300 mg.), b. p. 81-85°/9 mm, η_D^{30} 1.5297 ; λ_{max} 242mμ (ϵ, 12680).

Reduction of $\Delta^{4:8}$*-Hexalin to* $\Delta^{9:10}$ *-Octalin.*—To a mixture of the above diene (500 mg.), ether (10 c.c.) and liquid ammonia (80 c.c.), placed in a three-necked flask, lithium shavings (500 mg.) were added (2 mins.) with stirring. The deep blue solution was stirred for 20 minutes and then treated with absolute ethanol (5 c.c.) during 15 minutes. After the evaporation of ammonia, the residue was diluted with ice-water (100 c.c.) and the product taken up in petroleum ether (20 c.c. × 2), washed with brine and dried over activated silica gel. Removal of the solvent and distillation yielded $\Delta^{9(10)}$ *-octalin* (350 mg.), b. p. 75°/7 mm, $\eta_D^{26.5}$ 1.4370, which was characterised by the preparation of its *nitrosochloride* ; blue prisms (acetone), m. p. 92°, mixed m. p. with an authentic sample (Sukh Dev, *loc. cit* , 1954) was undepressed.

Action of Maleic Anhydride on $\Delta^{4:8}$*-Hexalin.*—A mixture of the diene (1.0 g.), maleic anhydride (0.98 g.) and dry benzene (15 c.c.) was refluxed for 20 hours. The solvent was distilled off from the yellowish reaction mixture and the residue treated with an excess of aqueous Na_2CO_3 solution and worked up as described elsewhere (Sukh Dev, this *Journal*, 1955, **32**, 330). A lot of polymerised neutral portion was obtained and the dicarboxylic acid (120 mg.) was recrystallised from benzene-petroleum ether mixture to give a white microcrystalline powder, m. p. 165-66°. (Found : C, 67.0 ; H, 7.4. $C_{14}H_{18}O_4$ requires C, 67.2 ; H, 7.2%).

The author is thankful to the National Institute of Sciences of India for the award of a Senior Fellowship during the tenure (1950-1953) of which this work was carried out.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore-3.

Received September 20, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

AZULENES AND RELATED SUBSTANCES. PART IX. *cyclo*PENTENOAZULENES: 1:2-TRIMETHYLENEAZULENE

By Sukh Dev

A synthesis of 1 : 2-trimethyleneazulene has been described.

The construction of a *cyclo*pentene system on to the azulene nucleus may be expected on geometrical considerations to alter the spectral characteristics of the resulting azulene derivative in a manner different from that observed in the case of the corresponding dialkylazulene. In order to investigate this aspect as well as to study other properties, it was decided to synthesise the various *cyclo*pentenoazulenes. Theoretically four such compounds (I-IV) are possible.

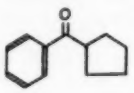
(I) (II) (III) (IV) (V)

The synthesis of the 3:4-isomer (II) has the additional interest that though it may be considered as an analogue of acenaphthene, it has two 5-membered rings fused on two vicinal bonds of *cyclo*heptatriene; the corresponding system in the case of benzene is unknown* (Braun and Anton, *Ber.*, 1929, **62**, 145; Braun and Reutter, *Ber.*, 1926, **59**, 1922). The present communication describes a synthesis of the 1:2-isomer (I); its light absorption properties will be discussed later, when the data on the other isomers are also obtained.

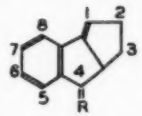
The 1:2-trimethyleneazulene (I) has been synthesised by the ethyl diazoacetate method of Plattner and co-workers (*Helv. Chim. Acta*, 1940, **23**, 907; 1941, **24**, 483; Gordon, *Chem. Rev.*, 1952, **50**, 141; Triebs, Kirchhof and Ziegenbein, *Fortsch. Chem. Forsch.*, 1955, **3**, 334). The *cyclo*pent[a]-indan-4-one (VII) required for this purpose was prepared by the procedure of Baker and Jones (*J. Chem. Soc.*, 1951, 787) with slight modifications which raised the overall yield from 45% to 60%. In connection with the preparation of (VII) the Nazarov cyclisation (*Bull. Acad. Sci. U.S.S.R. Cl. Sci. Chim.*, 1946, 633; 1947, 205; *J. Gen. Chem. Russia*, 1950, **20**, 2009, 2079, 2091) of benzoyl-Δ^1-*cyclo*pentene (VI) was also investigated; the cyclisation could not be effected by the usual phosphoric acid-formic acid reagent. Recently Braude and Forbes (*J. Chem. Soc.*, 1953, 2208) have also failed to synthesise a simple bi*cyclo*[3:3:0]-octane derivative by this procedure. The Clemmensen reduction of (VII) gave the corresponding hydrocarbon (VIII) in 84% yield (cf. Baker and

* The classical Baeyer's strain in the case of 3 : 4-*cyclo*pentenoazulene is less to the extent of 8.6° as compared to 1 : 7-*cyclo*pentenoindane (V). Experiments which may possibly lead to (V) are in progress.

Jones, *loc. cit.*) ; a crystalline byproduct could be obtained from the distillation residue. This byproduct, which is a hydrocarbon, is possibly derived from the pinacol corresponding to (VII) ; pinacolic reduction often occurs as a side reaction in the Clemmensen reduction (Sukh Dev, this *Journal*, 1949, **26**, 31).



(VI)



(VII : R=O)
(VIII : R=H_2)

(IX) (X)

The *cyclo*pent[a]-indane (VIII) on treatment with ethyl diazoacetate yielded a mixture of esters, which was hydrolysed to the correspondi ng mixture of acids. This on decarboxylation-dehydrogenation over Pd—C in a special apparatus (Sukh Dev, *ibid.*, 1955, **32**, 513) yielded the azulene (I) in a rather poor yield. The non-azulenic portion from this experiment was found to be chiefly acidic in character, which was shown to be resistant to decarboxylation and dehydrogenation. This indicates that the primary product of the Büchner reaction, which in the present case should have a *nor*caradiene structure (IX and other two isomers), is either resistant to base-catalysed (or thermal) isomerisation (Büchner and Hediger, *Ber.*, 1903, **36**, 3502 ; Darke and Sweeney, *J. Org. Chem.*, 1946, **11**, 67 ; Badger *et al.*, *J. Chem. Soc.*, 1951, 3456 ; cf. Reid *et al.*, *ibid.*, 1955, 1193) or isomerises preferentially to an acid of type (X) (Büchner and Schulze, *Annalen*, 1910, **377**, 259) ; the latter possibility is much more likely as the cases of the former type have been met with only polynuclear aromatic hydrocarbons, wherein *nor*caradiene structure is stabilised by the conjugative effect of *cyclo*propane ring (Badger *et al.*, *loc. cit.*), and moreover, in the present case a structure of type (IX) should have a strong tendency to pass into the quasi-aromatic azulene system on dehydrogenation.

Experimental

Melting and boiling points are uncorrected. The spectra were taken in 93% ethanolic solution on a Beckman DU spectrophotometer.

cyclo*Pent*[*a*]-*indan*-4-*one* (VII).—A mixture of *cyclo*pent-1-ene carboxylic acid (39.2 g., 0.35 *M* ; Sukh Dev, this *Journal*, 1956, **33**, 769) and purified thionyl chloride (40 c.c.) was heated on a steam-bath for 25 minutes and then the excess thionyl chloride removed from a bath at 80°-90° under 40-45 mm. The residual crude acid chloride was distilled to furnish a colorless liquid, b. p. 84-85°/30 mm, yield 44 g. (95.6%) (Baker and Jones, *loc. cit.*, record b.p. 65-67°/16 mm, yield 78%).

The above acid chloride was taken up in dry thiophene-free benzene (400 c.c.), cooled in ice and with stirring, and treated with coarsely powdered anhydrous aluminium chloride (133.4 g., 1 *M*) in three lots during ½ hour. The reaction mixture was stirred at the ice-temperature for 1½ hours and finally refluxed for another 1½ hours and left aside at room temperature (30°) for 2½ hours. The product was poured

onto ice and HCl; the benzene phase was separated and the aqueous part extracted with ether (75 c.c. × 2). The combined extracts after washing with HCl (1 : 1, 75 c.c.), water, aqueous sodium bicarbonate (5%, 100 c.c.) and brine was dried (Na_2SO_4). The solvent was stripped off and the residue carefully fractionated; after rejecting a purple-coloured fore-run (0.5 g., the colour gradually faded off), the required ketone (VII) was collected as a colorless liquid, b.p. 124-25°/2 mm, $\eta_D^{20°}$ 1 5710, d_D^{24} 1.103, yield 65%; λ_{max} 246 mμ (ε, 12610) (Baker and Jones, *loc. cit.*, record b.p. 145°/12 mm, η_D^{17} 1.5740, yield 58%).

cyclo*Pent*[*a*]-*indane* (VIII).—The above ketone (30 g.) in toluene (60 c.c.) was added to amalgamated zinc (from zinc wool 90 g. and mercuric chloride 9 g., water 135 c.c. and HCl 8 c.c.), covered with water (90 c.c.); HCl (conc., 180 c.c.) and glacial acetic acid (5 c.c.) were added and the mixture gently refluxed for 36 hours. A total of 300 c.c. of HCl (conc.) was added to the mixture over suitable intervals. The product was cooled, ether (75 c.c.) added and the light orange solvent layer separated, which was washed with brine (75 c.c. × 2) and dried (Na_2SO_4). The solvent was removed and the residue fractionated to afford (VIII) a colorless liquid, b.p. 92°/4 mm, $\eta_D^{30°}$ 1.5460, yield 23 g. (83.6%) (Baker and Jones, *loc. cit*, record b.p. 73-75°/1 mm, η_D^{17} 1.5511, yield 76%).

The distillation residue from the above experiment was taken up in benzene (12 c.c.) and the deep orange solution passed through a column of alumina, which was washed with petroleum ether. The deep yellow eluates on removal of the solvent furnished an orange viscous liquid, which on trituration with petroleum ether yielded a solid (1 g., m.p. 210-13°), crystallisation from benzene—*n*-hexane at 0° yielded almost colorless silky needles, m.p. 214-16°. (Found: C, 92.3; H, 7.7. $C_{24}H_{22}$ requires C, 92.9; H, 7.1 %).

Condensation of Ethyl Diazoacetate with cyclo*Pent*[*a*]-*indane*.—The above hydrocarbon (15.8 g., 0.1 *M*) was allowed to react with ethyl diazoacetate (EDA; 5 c.c.) exactly as described elsewhere (Sukh Dev, this *Journal*, 1955, **32**, 521). On working up, a fore-run of the unchanged hydrocarbon (12 g.) was obtained and the required ester was collected at 145-65°/2 mm as a red oil (3.0 g.). The recovered hydrocarbon was treated with EDA (4 c.c.) as before and this condensation was thus carried out for six times in all to finally yield a total of 14 g. of the condensation product and 4.0 g. of recovered hydrocarbon. This material was carefully fractionated to obtain the ester as a yellow liquid, b.p. 152-58°/2 mm, yield 9.0 g. (Found: C, 78.5; H, 7.5. $C_{16}H_{20}O_2$ requires C, 78.7; H, 8.2%).

The above ester (13.0 g.) was saponified by refluxing with potassium hydroxide (10 g. + water 20 c.c.) in alcohol (100 c.c.) for 10 hours. The red reaction mixture was diluted with water (300 c.c.) and extracted with ether (50 c.c. × 2) to remove the neutral material. The alkaline solution was acidified with HCl (conc.) and the liberated acid taken up in ether (40 c.c. × 3), washed with water and dried (Na_2SO_4). The solvent was flashed off and the residue fractionated to afford the acid as a dark yellow, exceedingly thick liquid, b.p. 165-70°/0.9 mm, yield 6.6 g. (Found: C, 78.0; H, 7.7. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.4%).

1 : 2-cyclo*Pentenoazulene* (I).—The dehydrogenation-decarboxylation of the above acid was carried out by the procedure described for 1 : 8-tetramethyleneazulene (Sukh Dev, *loc. cit.*). The catalyst bed was packed with 20% Pd—C (0.75 g.) mixed with freshly ignited asbestos (medium size ; 1.5 g.) and the above acid (6.0 g.) mixed with 20% Pd—C (0.5 g.) was slowly distilled through the hot bed of catalyst (320°-330°) under reduced pressure (35-45 mm) during ½ hour, exactly as described before. The blue (towards the end, bluish green) "distillate" was taken up in petroleum ether (15 c.c.) and chromatographed over alumina (Basic/I, 2.3 cm × 18 cm). The column was washed with petroleum ether till the main blue band was eluted out ; this was collected separately (*ca.* 75 c.c.). A very small bluish green band was left on the column which was washed out with ether (rejected). The column was allowed to dry overnight and next day washed with 5% aqueous Na_2CO_3 solution till no more acidic material could be extracted (125 c.c.).

Removal of the solvent from the blue eluates yielded the azulene (60 mg.). This was taken up in alcohol (3 c.c.) and treated with a solution of trinitrobenzene (60 mg.) in ethanol (3 c.c.). After several hours at room temperature and later at 15°, the crystals were collected, m.p 120-25°, yield 60 mg. This was recrystallised twice from alcohol (2 c.c.) to yield dark brown needles of the *trinitrobenzene complex*, m.p. 129-31°, yield 30 mg. These crystals dissolve in alcohol with a violet coloration. (Found : C, 60.0 ; H, 3.9 ; N, 10.97. $C_{19}H_{13}O_6N_3$ requires C, 59.8 ; H, 4.0 ; N, 11.0%).

Pure 1 : 2-*trimethyleneazulene* was regenerated from the complex (30 mg.) by chromatography over alumina as described previously (Sukh Dev, *loc. cit.*). The azulene was purified by distillation at 2 mm from a bath at 160-80° as a deep blue viscous liquid with a violet tinge. (Found : C, 92.6 ; H, 7.6. $C_{13}H_{12}$ requires C, 92.8 ; H, 7.1%).

The sodium carbonate extract on acidification and working up with ether, followed by distillation, yielded an acid (4.0 g.), b.p. 160-65°/0.5 mm. This on passing through the hot catalyst bed as above yielded only an almost colorless "distillate" which was found by chromatography to consist essentially of the unchanged acid ; the acid was found to be resistant to dehydrogenation-decarboxylation on distillation at atmospheric pressure with Pd—C.

Benzoyl-Δ^1*-cyclopentene* (VI) was prepared by the method of Fuson *et al* (*J. Amer. Chem. Soc.*, 1938, **60**, 1594). The material (b.p. 215-30°/3 mm, η_D^{25} 1.5650 yield 25%), purified by fractionation, was converted into the *semicarbazone* by the pyridine method ; two recrystallisations from alcohol yielded long, white prismatic needles, m p. 168-69°. (Found : N, 18.3. $C_{13}H_{15}ON_3$ requires N, 18.3%.

Pure benzoyl- Δ^1-*cyclo*pentene was regenerated from the semicarbazone (5.0 g., finely powdered) by refluxing it with oxalic acid (10 g. in 200 c.c. of water) and *n*-heptane (50 c.c.) for 3 hours (*i.e.* when all the semicarbazone had disappeared). Working up in the usual manner yielded the ketone as a colorless liquid, b.p. 125°/2 mm, η_D^{25} 1.5685, yield 90% ; λ_{max} 249 mμ (ε, 11800) (Baker and Jones, *loc. cit.*, record b.p. 143°/12 mm).

2 : 4-*Dinitrophenylhydrazone* (HCl method) was crystallised from alcohol to yield orange-red leaflets, m.p. 171-73°. (Found : N, 16.2. $C_{18}H_{16}O_4N_4$ requires N, 15.9%).

[Baker and Jones, *loc. cit.*, record m.p. 162-63° ; this discrepancy in the melting point is understandable since Baker and Jones' procedure for the synthesis of (VI) may be expected to yield a product contaminated to a certain extent with the cyclised ketone (VII)].

When pure benzoyl*cyclo*hexene (1.0 g.) was treated with a mixture of formic acid-phosphoric acid, according to the details of Braude and Forbes (*loc. cit.*), the ketone (0.7 g.) was recovered as established by the m.p. (166-68°) of its semicarbazone, which was unaltered on admixture with an authentic sample.

The author is grateful to the National Institute of Sciences of India for the award of a Senior Fellowship (1950-53) during the tenure of which this work was carried out.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore-3.

Received September 20, 1956

[Jour. Indian Chem. Soc., Vol. 34, No 2, 1957]

ACTION OF SULPHUR DIOXIDE WATER ON PERMANGANATES OF BARIUM AND SILVER

By Kundan Lal and Chander Mehra

Action of normal sulphurous acid on 1% solution of barium permanganate and 0.5% solution of silver permanganate has been studied.

When normal sulphurous acid reacts with solutions of barium and silver permanganates, about 88-89% of it is oxidised to various sulphur acids (SO_4^{2-} and $S_2O_6^{2-}$). The rest is lost due to volatilisation of sulphur dioxide during the preparation and addition of normal sulphurous acid. Free sulphuric acid, metal sulphate and dithionate and manganese sulphate are the various products of reaction. A precipitate of the general composition $xRO.yMnO.zMnO_2$ is formed. With the increasing volumes of the sulphurous acid the amount of precipitate decreases until it vanishes completely. Finally, total manganese is accounted for as sulphate, and the metal, as sulphate and dithionate both.

Previously, the action of normal sulphurous acid on permanganates of calcium and ammonium (Lal and Singh, this *Journal*, 1955, **32**, 547 ; Lal and Mehra, *ibid.*, 1956, **33** 668) has been reported. In the present investigation the action of normal sulphurous acid on permanganates of barium and silver has been attempted.

Experimental

Barium Permanganate.—Barium permanganate employed in the present investigation was prepared by the method recommended by Muthmann (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XII, p. 333, Longmans, Green & Co., London, 1947). It was filtered through an asbestos filter and preserved in a well-stoppered bottle in dark. Its purity was tested and exactly an 1% solution, required for the present investigation, was prepared by dilution.

The intermediate stage of the reaction was studied by adding freshly prepared normal sulphurous acid to barium permanganate solution (50 c.c., 1%), dropwise in duplicate, until the purple colour of the permanganate was just discharged. Only sulphate and dithionate were detected in the filtrate. It gave no tests for barium, manganese, thiosulphate and higher thionates.

The sulphate content was estimated as barium sulphate in cold (Mitchel, "Modern Methods of Chemical Analysis", p. 136) and the dithionate by oxidising it with potassium bromate and HCl (conc.) as previously done (Lal and Singh, *loc. cit.*). The total normality of the acids, determined by alkali titration, was found to correspond with the sum of those calculated from sulphate and dithionate estimations (H_2SO_4, 86.8% and $H_2S_2O_6$, 13.2%), thus indicating that sulphate and dithionate, both, must be present as free acids only.

The dark brown precipitate was found to consist of hydrated manganese dioxide, manganese oxide, barium oxide and barium sulphate. Manganese dioxide was estimated by the method used by Mohammed and Ahluwalia (this *Journal*, 1941, **18**, 309). Barium sulphate was separated and estimated from the remaining solution. Total manganese was

removed as sulphide from the solution left over and then estimated as pyrophosphate (Gooch and Austin, *Z. anorg. Chem.*, 1898, **18**, 339). The amount of barium present as barium oxide in the precipitate was estimated as barium sulphate from the solution after removal of the manganese sulphide. The manganese oxide content was determined from the total manganese and that corresponding to manganese dioxide. The molar ratio of $BaO : MnO : MnO_2$ came out to be 1 : 4 : 19.

The reaction was further studied with one-half and three-fourth of the volume of the *N*-sulphurous acid required for the intermediate stage. The amounts of unchanged MnO_4^- were estimated by titrating against ferrous ammonium sulphate solution. Barium being absent, the MnO_4^- was accounted for as $HMnO_4$ in the filtrates. Small amounts of dithionate also were produced in these experiments. From the results the molar ratio of $BaO : MnO : MnO_2$ in the precipitate appears to be 1 : 4 : 19 again.

More experiments were repeated with the increasing volumes of the *N*-sulphurous acid. Just after the intermediate stage, formation of some manganese sulphate was also noticed, and subsequently an increase in the amount of this product continued until the total amount of manganese was converted into manganese sulphate (expt. No. 6, Table I). The acidic character of the filtrate became more and more pronounced due to the formation of increasing quantities of sulphuric and dithionic acids. Formation of any thiosulphate and higher thionates was not detected in these experiments also. The intensity of the colour as well as the amount of the precipitate formed during this stage was found decreasing with the increasing volumes of the sulphurous acid. A regular decrease in the quantity of manganese dioxide with a corresponding increase in the manganese oxide content of the precipitate was observed. Finally the product became absolutely white and free from oxides of manganese and barium. It was only barium sulphate. In expt. Nos. 4 and 5, the molar ratio of $BaO : MnO : MnO_2$ comes out to be 1 : 7 : 21 and 1 : 23 : 27 respectively against 1 : 4 : 19 in expt. Nos. 1 to 3, Table I.

In expt. No. 6, the total amounts of manganese and barium, both, are accounted for as sulphate, the former remaining in the solution and the latter, due to its insoluble character, in the precipitate. A decrease in the sulphuric acid content in expt. No 6 further suggests that after the complete reduction of manganese dioxide to manganese oxide, the latter perhaps reacts completely with sulphuric acid according to the equation,

$$MnO + H_2SO_4 = MnSO_4 + H_2O \qquad (1)$$

showing thereby that manganese dioxide acts as a negative catalyst in the reaction. The analytical values of this experiment may be expressed by the equation,

$$4\,Ba(MnO_4)_2 + 21\,H_2SO_3 = 4\,BaSO_4 + 8\,MnSO_4 + H_2S_2O_6 + 7\,H_2SO_4 + 13\,H_2O \quad \ldots \quad (2)$$

Again purified sulphur dioxide gas was passed through barium permanganate solution (50 c.c., 1%) for a long time. The precipitate consisted of barium sulphate only and the filtrate gave tests for sulphate, sulphite (from unchanged sulphurous acid), dithionate and manganese. Formation of any thiosulphate and higher thionates was not detected.

TABLE I

Products of reaction with N-H_2SO_3 + $Ba(MnO_4)_2$.

Total Ba added = 0.1827 g. Total Mn added = 0.1467 g.

(The values inserted being mean of the duplicate experiments).

Expt. No.	H_2SO_3 added.	$Ba(MnO_4)_2$ (% decomp.).	$BaSO_4$.	$MnSO_4$.	$H_2S_2O_6$.	H_2SO_4.	BaO : MnO : MnO_2. (mol. ratio)	BaO : MnO : MnO_2. (mol. ratio, approx).
1	5.00 c.c.	53.35	0.2960 g.	Nil	0 0198 g.	0.0682 g.	1 : 4.38 : 18.59	1 : 4 : 19
2	7.00	79 69	0.2894	,,	0.0270	0.1721	1 : 4 31 : 18 81	1 : 4 : 19
3	9.85	100.00	0 2858	,,	0 0383	0.2539	1 : 3 94 : 18.79	1 : 4 : 19
4	11.95	,,	0.2960	0.1178 g.	0 0466	0.2589	1 : 7.28 : 20.59	1 : 7 : 21
5	14 05	,,	0.3068	0 2194	0.0536	0.2733	1 : 23.24 : 27 01	1 : 23 : 27
6	16.40	,,	0.3098	0 4027	0 0572	0.2479	Nil	Nil

Silver Permanganate.—A freshly prepared solution of normal sulphurous acid was added likewise to silver permanganate solution (100 c.c., 0.5%) till the colour of the permanganate was just discharged. The filtrate gave tests for silver, sulphate and dithionate only. It was distinctly acidic due to the formation of sulphuric acid. No manganese was detected in the filtrate. Silver, quantitatively estimated as AgCl, was accounted for as sulphate and dithionate, both, which were estimated respectively as in the earlier section. The analytical data are recorded in Table II. The dark brown precipitate on quantitative analysis gave values of 1 : 1 : 6 for the molar ratio of $Ag_2O : MnO : MnO_2$. The compound by analogy may be called silver manganous hexamanganite.

The investigation was continued with one-half and three-fourth of the normal sulphurous acid required for the intermediate stage (expt. Nos 1 and 2, Table II). Each filtrate contained unchanged silver permangnate, silver dithionate and some sulphuric acid. In the precipitates the same compound, *i.e.* silver manganous hexamanganite, was observed throughout.

TABLE II

Products of reaction with N-H_2SO_3 + $AgMnO_4$ (100 c.c., 0.5%)

Total Ag added = 0.2379 g. Total Mn added = 0.12115 g.

(The values inserted being mean of the duplicate experiments).

Expt No.	H_2SO_3 added	$AgMnO_4$ (% decomp.).	Ag_2SO_4.	$MnSO_4$.	$Ag_2S_2O_6$.	H_2SO_4.	$Ag_2O : MnO : MnO_2$. (mol. ratio).	$Ag_2O : MnO : MnO_2$. (mol. ratio, approx.).
1	4.20 c.c.	54.57	0.1471	Nil	0 0200 g.	0.1257g.	1 : 1.20 : 6.45	1 : 1 : 6
2	6.30	82 67	0.2133	,,	0.0397	0.1849	1 : 1.095 : 6 17	1 : 1 : 6
3	8.50	100 00	0.2581	,,	0.0469	0.2641	1 : 1.25 : 6.23	1 : 1 : 6
4	10 70	,,	0.2581	0.1249 g.	0.0578	0.2677	1 : 2.25 : 4.92	1 : 2 : 5
5	12.90	,,	0.2589	0.2391	0 0992	0.2676	1 : 21.22 : 5.33	1 : 21 : 5
6	13 40	,,	0.2583	0 3326	0.1024	0.2295	Nil	Nil

Lastly, with the increasing volumes of normal sulphurous acid (expt. Nos. 4, 5 and 6, Table II), the value of silver sulphate was found to be constant and a regular increase in the amount of silver dithionate was observed. The presence of sulphuric acid was detected in each experiment. The molar ratio of $Ag_2O : MnO : MnO_2$ comes out to be 1 : 2 : 5 and 1 : 21 : 5 respectively (expt. Nos. 4 and 5). In expt. No. 6 no precipitate was left. The total amount of silver was accounted for as sulphate and dithionate, both, and that of manganese, as sulphate only. A decrease in the sulphuric acid content, in this investigation also, supports the view represented by equation (1). The reaction in expt. 6 may be represented by the equation,

$$8\ AgMnO_4 + 21\ H_2SO_3 = 3\ Ag_2SO_4 + 8MnSO_4 + Ag_2S_2O_6 + 8\ H_2SO_4 + 13\ H_2O \quad \ldots \quad (3)$$

Further, purified sulphur dioxide gas was passed through silver permanganate solution (100 c.c., 0.5%) till the dark brown precipitate first formed was completely acted upon. The clear solution showed tests for sulphate, sulphite (due to unchanged sulphurous acid), dithionate, manganese and silver only. Any thiosulphate and higher thionates were not formed in this reaction also.

CHEMISTRY DEPARTMENT,
PANJAB UNIVERSITY,
HOSHIARPUR.

Received July 2, 1956

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

CHEMICAL STUDIES OF SOME INDIAN LAURACEAE FATS. PART I

By S. A. Narang and S. V. Puntambekar*

The chemical composition of the mixed fatty acids including unsaponifiable matter of the five Lauraceae fats have been studied by the modified method consisting of crystallisation of trilaurin of the fats from alcohol and of separation and identification of the individual fatty acids in the alcohol-soluble portion of the fats in the usual manner.

The glyceride composition of the Lauraceae fats has been arrived at by employing the two Kartha's methods for their estimation.

The seeds of the plants of Lauraceae family contain a large quantity of a fatty oil (Kirtikar and Basu, "Indian Medicinal Plants", 1918, p. 1103). Puntambekar and Krishna (this *Journal*, 1933, **10**, 395) investigated the fat obtained from *Actinodaphne hookeri* Meissn. in 48% yield and found it to consist of the glycerides of 96% lauric acid and 4% oleic acid. Isolation of the free trilaurin or lauric acid from the fat has been a very simple matter. Not many examples are known where a fat from a natural source has been found to consist mostly of a glyceride of a simple fatty acid, and therefore the investigation on the fats from other species of this family has been of further academic interest. It has also commercial interest as a source of excellent detergent, satisfactory lubricating agent for watches and other delicate machines and as a wetting agent for insecticidal preparations. An opportunity was therefore taken to study the component fatty acids and the glycerides of the following species of Lauraceae family: *Litsaea chinensis* Lamk, *Litsaea citrata* Blume, *Litsaea lanuginosa* Nees, *Litsaea zeylanica* Nees and *Actinodaphne angustifolia* Nees.

Besides the work of Puntambeker (this *Journal, Ind & News Ed.*, 1938, **1**, 21) on the physico-chemical characteristics of the fats from the seeds of the above mentioned species, the only other work on them has been reported by Gunde and Hilditch (*J. Chem. Soc.*, 1938, 1610) and Kane (*Indian Soap J.*, 1951, **17**, 52). The present investigation has been carried on the old samples of the fats, and so variations in acid and iodine values have been experienced due to their partial hydrolysis. In all cases the fats were from samples expressed from kernels and did not contain any pericarp oil.

Experimental

The physico-chemical characteristics of the fats obtained from the above mentioned samples have been determined by the commonly used methods and tabulated below.

* At present Director, Indian Lac Research Institute, P. O. Namkum, Ranchi.

TABLE I

Physico-chemical characteristics of the Lauraceae fats.

	L. chinensis.	*L. citrata.*	*L. lanuginosa.*	*L zeylanica.*	*Actinodaphne angustifolia.*
Colour ...	Pale yellow	Pale yellow	Light brown	Pale yellow	Pale yellow
M. P. ...	39-41°	40-42°	39-41°	35-36°	42-45°
Sp. gr. ...	0.915/40°	0.9118/35°	0.9234/35°	0.9230/30°	0.9209/40°
Ref. ind. at 40°	1 4451	1.4403	1.4452	1 4451	1.4403
Iodine value (Hanus)	4.45	5.6	9.72	15 1	7.1
Sapon. value	257.71	264.25	260.0	258 6	251.85
Ester value ...	220.5	196.35	191.4	171.66	225 95
Acid value ...	37.21	67.9	69.5	86.94	25.9
Hehner value(%)	91.9	88.7	88.1	82.35	86.2
Acetyl value ...	23.8	17.35	19.25	16.74	20.32
Unsap. matter (%)	1.25	1.7	1.3	1.3	1 25
Trilaurin crystallised out(%)	73.8	70.4	54.0	...	83 4

Composition of the Fats and their Fatty Acids.—The fats when crystallised from a large volume of alcohol were obtained in fine silky needles, m.p. 45-46°, sap. value, 264 and I. V. 1.1. On saponification, they gave an acid which on crystallisation from dilute alcohol melted at 43-44° and had a mean M. W. of 200.5. The mixed melting point of this acid with an authentic sample of lauric acid remained unchanged. These facts indicated that the fats were mostly trilaurin.

Component Fatty Acids

For the determination of the composition of the fatty acids, as much as possible of the sparingly soluble trilaurin of iodine value 0.0 was removed by crystallisation of the fats from 95% alcohol and the residue (glycerides, soluble in alcohol) left in the mother-liquor was saponified and separated into 'solid acids' and 'liquid acids' by Twitchell's method modified by Hilditch ("The Chemical Constitution of Natural Fats", 1949, p. 468).

Liquid Acids.—A portion of the 'liquid acids' on bromination (Lewkowitsch, "Chemical Technology and Analysis of Oils and Fats", 1921, Vol I, p. 581) did not yield any of the hexabromides and tetrabomides, thus showing the absence of linolenic and linoleic acid respectively. Thus, only the possibility of formation of dibromide of the oleic acid remained and its presence was confirmed in the residual brominated product after removal of the petroleum ether by distillation under vacuum, as described below

TABLE II

Mixed fatty acids of the alcohol-soluble glycerides.

	L. chinensis.	*L. citrata.*	*L. lanuginosa.*	*L. zeylanica.*	*Actinodaphne angustifolia.*
Wt. of the fat taken(g.)	260.0	110.0	92.0	69.0	96.4
Wt. of the residual fat portion, soluble in alcohol, obtained (g.)	68.0	33.6	42.3	...	16.0
I. V. of the mixed fatty acids of the glycerides portion.	7.61	7.5	21.65	22.0	15.9
Mean M. W. of the mixed fatty acids of soluble glycerides portion.	206.0	208.0	215.0	211.0	213.0
I. V. of the solid acids.	3.48	4.14	6.63	6.0	6.07
Mean M. W. of the solid acids.	203.5	203.0	204.0	205.0	205.7
I V. of the liquid acids.	20.95	21.3	34.4	34.0	20.6
Mean M. W. of the liquid acids.	217.7	218.0	225.0	221.0	222.8
% Solid acids.	60.1	66.7	45.2	60.7	49.6
% Liquid acids.	39.9	33.3	54.8	39.0	50.4

The brominated product was converted into the sodium soap by neutralising its alcoholic solution with dilute aqueous NaOH solution under constant stirring until a clear solution was formed. To this was added an aqueous solution of $MgSO_4$ with constant stirring to precipitate the magnesium soaps of dibromo-oleic as well as lauric acids and other lower saturated fatty acids that might be present. The magnesium soaps were filtered, washed, dried and dissolved in 50% hot ethanol in which the magnesium laurate and other lower saturated fatty acid salts easily dissolved (Lewkowitsch, *ibid.*, p. 159), leaving behind magnesium dibromo-oleate which was again treated with 50% hot ethanol This process was repeated 3 to 5 times to obtain a pure sample of the magnesium dibromo-oleate. The free dibromo-oleic acid was liberated from this product by heating it with an excess of mineral acid (dil. H_2SO_4). The upper layer of the separated fatty acid was extracted with ether. The ethereal solution was washed with water to free it from the mineral acid and the ether was distilled off. The last traces of ether was removed under vacuum and the dibromo derivative of the oleic acid was dried by placing it overnight in a vacuum desiccator. The bromine content of dibromo-oleic acid (found : 36.76% ; calc. 36.18%) was determined by Stephanow's method (Coleman and Arnall, "Preparation and Analysis of Organic Chemistry", 1926, p. 287). All the alcoholic filtrates were combined and concentrated to a small volume on a water-bath to remove most of the ethanol. The residual magnesium soap was treated with H_2SO_4 (dil.) and the mixture was heated on a water-bath till a clear fatty layer was formed on the top. This was taken up in ether, washed free of the mineral

acids, dried over anhydrous $MgSO_4$ and the ether distilled off. The fatty acid on crystallisation from dilute acetone melted at 43-44° and was identified as lauric acid by its mixed melting point with an authentic sample.

The presence of the oleic acid was further confirmed by the isolation of dihydroxystearic acid (m. p. 129-30°, mean M. W. 318.0) in the oxidised product of another portion of the liquid fatty acids by Lapworth and Mottram's method (*J. Chem. Soc.*, 1925, 1628).

Solid Acids.—The solid acids were converted into their methyl esters by treating with 5 times of methanol containiug 3.5% HCl by the usual manner. The neutral methyl esters were fractionally distilled under reduced pressure with the following results. The acids were identified by subjecting them to recrystallisation from dilute ethanol and dilute acetone. These were confirmed as lauric acid by their melting point with an authentic sample. No other saturated acids could be detected. The following fractions were obtained in each case.

TABLE III

Name of the fat	Fr.	B.P.	S.E.	I.V.	Wt./g.	Methy lauratel.	Methyl oleate.
a. L. chinensis	S_1	120-125°	208.4	1.8	1.6158	1.6158 g.	...
(29 2 g.	S_2	125-132°	211.7	1.9	6.7337	6.7337	...
of the methyl	S_3	132-137°	213.5	1.8	11.9012	11.9012	...
esters dis-	S_4	137-142°	214.3	1.4	6.4884	6.4884	...
tilled at 9 mm.)	S_5	142-160°	217.1	2.0	1.0290	1.0062	0.0228 g.
	Residue	...	...	...	1.0413	1.0184	0.0229
	Loss	...	...	...	0.3906	...	...
	Total	...	...	...	29.2000	28.7637	0.0457
b. L. citrata							
(11.25 g.	S_1	Up to 120°	211.0	1.5	1.673	1.673	...
of the methyl	S_2	120-124°	214.0	1.0	8.978	9.978	...
esters distil-	Residue	...	...	...	0.486	0.486	...
led at 5 mm.)	Loss	...	...	...	0.123	...	...
	Total	...	...	...	11.250	11.137	...
c. L. lanuginosa	S_1	110-120°	213 0	1.1	3.073	3.073	...
(13.0757 g.	S_2	120-125°	215.0	1.2	3.0287	3.0287	...
of the methyl	S_3	125-130°	225.5	20.1	6.0095	4.7845	1.225
esters dis-	Residue	...	...	...	0 8293	0.6411	0.1882
tilled at 4 mm)	Loss	...	...	...	0.1352	...	...
	Total	...	...	...	13.0757	11.5273	1.4132
d. L zeylanica	S_1	105-110°	218 0	1.5	1 9486	1.8426	0.106
(30.0 g. of	S_2	110-115°	221.0	10.0	12.659	11.202	1.457
the methyl	S_3	115-120°	222 0	10 5	13 8545	12.0554	1.7991
esters dis-	Residue	...	...	...	1 3961	1.2320	0.1641
tilled at 2 mm.)	Loss	...	...	...	0.1418	...	...
	Total	...	...	...	30.00	26.332	3.5252

e. Actinodaphne angustifolia: The amount of the solid acids obtained was insufficient to prepare their methyl esters and their subsequent fractional distillation purpose. The solid acids on crystallisation from dilute alcohol gave a product which was yellow in colour and on recrystallisation from dilute acetone yielded a product, m.p. 43-44° and mean M.W 200.1 This was identified as lauric acid.

Calculation of the Component Fatty Acids of Litsaea chinensis *Seed Fat*

An example is given below to show how the component fatty acids of a Lauraceae fat have been calculated :

1. Amount of the mixed fatty acids obtained from 68 g. of alcohol-soluble fat = 58.0 g.
2. Amount of 'solid acids' obtained by Twitchell's method from 55.0 g. of the mixed fatty acids = 33.0 g.
3. Amount of 'solid acids' present in 58.0 g. of the mixed fatty acids (1) $= \frac{33.0 \times 58.0}{55.0}$ $= 34.79$ g.
4. Amount of the 'liquid acids' obtained from 55.0 g. of the mixed fatty acids by Twitchell's method = 22.0 g.
5. The amount of 'liquid acids' present in 58.0 g. of the mixed fatty acids (1) $= \frac{22.0 \times 58.0}{55.0}$ $= 23.21$ g.
6. Amount of methyl laurate obtained by the fractional distillation of 29.2 g. of 'solid acids' esters = 28.76 g.
7. Equivalent quantity of lauric acid in (6) $= 28.76 \times 0.9345$ $= 26.87$ g.
8. Amount of methyl oleate obtained from 29.2 g. of 'solid acids' esters = 0.0457 g.
9. Equivalent quantity of oleic acid (8) $= 0.0457 \times 0.9527$ $= 0.043$ g.
10. Amount of the lauric acid present in 34.79 g. of 'solid acids' $= \frac{26.87 \times 34.79}{26.91}$ $= 34.72$ g.
11. Amount of oleic acid in 34.79 g. of 'solid acids' = 0.07 g.
12. Amount of oleic acid in 'liquid acids' (4) 22.0 g. of I. V. 20.85 = 5.18 g.
13. Amount of oleic in 23.21 g. of 'liquid acids' (5) $= \frac{5.18 \times 23.21}{22.0}$ $= 5.464$ g.
14. Amount of lauric acid in 'liquid acids' (5) $= (23.21 - 5.464)$ $= 17.746$ g.
15. Total lauric acid in mixed fatty acids (1) = 34.72 (in 'solid acids') + 17.746 (in 'liquid acids') $= 52.466$ g.
16. Total oleic acid in mixed fatty acids (1) $= 5.464 + 0.07$ $= 5.534$ g.

17. Trilaurin obtained by crystallisation from 260.0 g. of fat = 192.0 g.

18. Amount of lauric acid present in 192.0 g. of trilaurin $= \frac{600 \times 192.0}{638}$
$= 180.4$ g.

19. Total lauric acid in mixed fatty acids of the whole fat = (180.4 + 52.466)
= 232.866 g.

20. Total mixed fatty acids + U.S.M. 232.866 (lauric acid)
+ 5.534 (oleic acid) + 3.0 U.S.M = 241.4 g.

21. % Lauric acid in (20) = 96.27

22. % Oleic acid in (20) = 2.32

23. % Unsaponifiable matter = 1.41

Components:

Lauric acid	= 96.27%
Oleic acid	= 2.32%
Unsaponifiable matter	= 1.41%

TABLE IV

Component fatty acids of the five Lauraceae fats.

	Lauric acid.	Oleic acid.	Unsap. matter.
L. chinensis	96.27%	2.32%	1.41%
L. citrata	96.06	2.15	1.79
L. lanuginosa	88.05	10 41	1.54
L. zeylanica	76.70	21 90	1.40
A. angustifolia	96.60	2.10	1.30

Unsaponifiable Matter.—The sterol content of the unsaponifiable matter was estimated in each case by the digitonin-addition method (Lewkowitsch, *loc. cit.*, p. 607). The filtrate from the above operation was evaporated to dryness. The residue was found to be mainly consisted of waxes, hydrocarbons and other higher alcohols. The acetyl derivative of sterol was prepared, m. p. 119-20°, and confirmed as sitosterol which is commonly present in the vegetable oils and fats.

Component Glycerides

Two quantitative methods have been used for the estimation of the glycerides of the Lauraceae fats, namely, (*a*) oxidation of the neutral fat by acetone-acetic acid-permanganate method (Kartha, *J. Sci. Ind. Res.*, 1953, **12A**, 504), used in the case of *L. chinensis*, *L. lanuginosa* and *A. hookeri*, and (*b*) examination of the melting points of fats and their mixed fatty acids (Kartha, *ibid.*, 1954, **13A**, 72) used in the case of *L. chinensis*, *L. citrata*, *L. lanuginosa*, *L. zeylanica* and *A. angustifolia*.

TABLE V

[By method *a*]

	L. chinensis.	*L. lanuginosa.*	*A. hookeri.*
Wt. of the neutralised fat taken for oxidation (g)	13 198	12 26	10 648
Wt of the GS_3 * obtained (g.)	12.53	9.81	10 1
I.V. of the GS_3 *	1.0	0.5	1.0
No precipitate formed in the carbonate extract.	Showed the	absence of	GS_2U.
Acidified the above carbonate soln. with dil. H_2SO_4, staturated with common salt and extracted with ether, and the ether distilled off.	No residue left, thus showed the absence of GSU_2.		
% GS_3 (found)	96 0	80.0	95 0
% Trilaurin (calc.)	94 9	79.4	93 9
% Oleodilaurin (calc.)	1.1	0.6	1.1
% Triolein (calc.)	2.7	18.7	3.1
Unsaponifiable matter	1.3	1 3	1.9

* Triglycerides of saturated fatty acids.

Examination of the M.P. of Fats and their Mixed Fatty Acids.—It has been shown by Kartha (*loc. cit.*) that GS_3 content of the natural fat is generally a function of the saturated acid content and their difference in m.p. of fats and their mixed fatty acids. All biological and other factors influencing the regulation of chance distribution in the natural fat find expression in the difference of m.p. between the fats and their mixed fatty acids. The results are shown in Table VI.

TABLE VI

Tri-saturated glycerides content of Lauraceae fats according to the present method of D.m.p. value (method b).*

Lauraceae fats	S% (mol.) Expt	GS_3. Chance % (mol) graph.	Melting points. Fats	Mixed fatty acids.	D.m.p value (approx.).	GS_3 content	GS_3%. (mol.) Calc.
Litsaea chinensis	98 5	96.0	105°F	100°F	0	1.0	96.0
Litsaea citrata	98.2	95.0	107°	103°	0	1.0	95.0
Litsaea lanuginosa	90.4	75.0	105°	100°	0	1.0	75.0
Litsaea zeylanica	84.4	59.0	97°	93°	0	1.0	59.0
Actinodaphne angustifolia	98.4	95.0	113°	109°	0	1 0	95.0

* D.m.p. value of fat has been termed as depression of melting point of fat as compared to the chance distribution from the same component acids and mathematically may be termed as (4+m.p. of the mixed fatty acids−m.p. of fat)°F.

DISCUSSION

Physico-chemical Constants.—The samples of the fats used in the present investigation were old and had been in storage since 1938; therefore some variations in acid, iodine, saponification, Hehner and acetyl values have been recorded in each

case. This might be attributed to the possibility that these fats have become rancid due to long storage with the formation of some free fatty acids and water-soluble degradation products of the constituent glycerides. Thus, the higher acid value found in each case is due to the presence of free fatty acids. Similarly, the slightly lower iodine value is due to the little breakdown and disappearance of some of the oleic acid glycerides to form the degradation products having no unsaturation. The Hehner values, lower than the theoretical values, could be explained by the fact that some of the lauric acid passed out in the soluble form into washings during the liberation of free acids from the saponified fat. Similar effect with respect to this value was also experienced by Schroeder (*Arch. Pharm.*, 1905, **243**, 628) and Puntambekar (*loc.cit.*) during the investigation of the seed fats of *Litsaea chinensis* and *Actinodaphne hookeri* respectively. The high acetyl value indicates the presence of free hydroxyl groups in the glycerol part of the fats due to the partial hydrolysis of the glycerides brought about by the rancid conditions attained by long storage, thereby setting one or two hydroxyl groups of the glycerol radical free.

Method of Estimation of Component Fatty Acids of Fats.—Owing to the preponderance of a single fatty acid (lauric 95%) in the mixed acid and in order to be able to definitely characterise the small amount of unsaturated acid present in them, the method adopted in the case of the seed fats of *Litsaea chinensis, Litsaea citrata, Litsaea lanuginosa* and *Actinodaphne angustifolia* was to separate out the crystallisable trilaurin from the fats by crystallisation from 95% ethanol, then to concentrate any free fatty acids or glycerides of oleic acid in the alcohol-soluble residual fatty portion. The alcohol-soluble fatty portion is subesquently treated as a new fat and subjected to saponification, liberation of the mixed fatty acids by Twitchell's method, conversion of the 'solid acids' into methyl esters and their fractional distillation under reduced pressure to isolate individual acids and the identification of the unsaturated acid in liquid acids by oxidation and bromination methods. In this way, it became quite simple to identify the relatively large amount of oleic acid in the alcohol-soluble portion of the fat as compared to in the original sample.

Bromination.—The identification of the oleic acid in the presence of a large quantity of low-molecular weight saturated acid, *i.e.* lauric acid, has been satisfactorily brought about by the bromination of the liquid acids (3-5 g.) and the separation of lauric acid from the brominated product by the magnesium salt formation of the total acids and their repeated crystallisation from 50% hot ethanol to get a pure sample of magnesium dibromo-oleate. The free dibromo-oleic acid was liberated from the product by heating it with dilute sulphuric acid and finally the bromine content of dibromo-oleic acid was determined by Stephanow's method.

Sincere thanks of the authors are due to Dr. Sadgopal, Senior Research Officer-in-charge, Chemistry of Forest Products Branch, Forest Research Institute, Dehra Dun, for the keen interest he has taken during the investigation and also to the President, F.R.I. and Colleges, Dehra Dun, for allowing the facilities to one of the authors (S.A.N.) for this work to be carried out in this Institute.

CHEMISTRY OF FOREST PRODUCTS BRANCH,
FOREST RESEARCH INSTITUTE, DEHRA DUN.

Received February 1, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No.2, 1957]

CHEMICAL STUDIES OF SOME INDIAN LAURACEAE FATS. PART II. THE FATTY OIL FROM THE SEEDS OF *CINNAMOMUM CAMPHORA* NEES.

By S. A. Narang and S. V. Puntambekar

The fat from the seeds of *Cinnamomum camphora* Nees. has been found to contain the glycerides of lauric, capric and oleic acids together with a small quantity of unsaponifiable matter.

Cinnamomum camphora Nees. (N. O. Lauraceae) is a large, handsome, evergreen tree attaining in its natural habitat a height of 100 ft. and a girth of 6 to 8 ft., leaves coraceous shining, 3 to 4 inches long, smelling strongly of camphor when crushed. The chief product of the tree, however, is camphor, used largely in the manufacture of celluloid and smokeless powders and also to some extent in drugs and insectifuge. In Northern India, the leaves are shed round about February-March and in March-April, the trees are covered with masses of pale fragrant leaves. The fruit ripens in October. The fruit is dark green, rather dry, one-seed berry is of about 0.3 inch in diameter and turns black after ripening.

The seeds collected from trees in New Forest, Dehra Dun, have been reported to yield 59.0% of a pale yellow fat on kernels and it has been studied for its physico-chemical constants by Puntambekar (this *Journal, Ind. & News Ed.*, 1938, **1**, 21). The preliminary studies on this fat have also been reported by Sekimoto and Hirao (*J. Oil Chem. Soc., Japan*, **2**, 4) and Tsujimoto (*J. Coll. Eng.*, Tokyo, 1908, **4**, 75). It was therefore thought desirable to record the results of a detailed examination of this fat.

Experimental

The sample of the fat used in the present investigation was old and had been in storage since 1938 ; therefore, some variations in acid, iodine and saponification values from that of the fresh fat have been recorded.

Table I

Physico-chemical characteristics of the fat.

	Values obtained by			Values obtained by	
	Present authors.	Puntambekar.		Present authors.	Puntambekar.
Colour	Pale yellow	Pale yellow	Acid value	16.3	1 4
M. P.	25-26°	...	Sapon. value	299 93	272.3
Sp gr. at 25°	0.924	0.925	Ester value	283.0	270 9
Ref. index at 25°	1.4444	1.4442	Hehner value	88.45%	...
I. V. (Hanus)	3.6	4.0	Unsap. matter	1.4	...

The component fatty acids from *Cinnamomum camphora*, Nees. fat have been quantitatively separated by Twitchell's modified lead-salt method (Hilditch, "The Chemical Constitution of Natural Fats", 1949, p. 468) into groups consisting mainly of saturated and unsaturated acids respectively, followed by conversion of each group into methyl esters, and their systematic fractionation under vacuum. The results obtained are: mean M. W., 195.0; neutralisation value, 286.0; I. V. (Hanus), 3.87; 'solid acids', 46.15% and 'liquid acids', 53.85%.

The fat (92.0 g.) was saponified with alcoholic potash. The alcohol was distilled off, the resultant soap dissolved in water and the mixed acids were liberated by the addition of HCl (conc.). The free fatty acids were washed with warm water and neutralised with 10% KOH solution. The soap solution was concentrated, incorporated with washed filter paper pulp and the resulting soap was dried, powdered and extracted with ether in a soxhlet to remove unsaponifiable matter. The mixed fatty acids (80.0 g) were liberated from the residual soap and 78.0 g. of these was separated into 'solid and liquid acids' by the well-known Twitchell's modified method (Hilditch, *loc. cit.*).

Solid Acids.—The 'solid acids' (26.0 g) were converted into methyl esters in the usual manner by treating with 3% methyl alcoholic hydrochloric acid. After distilling off most of the methyl alcohol, the esters were washed with 5% Na_2CO_3 and finally with distilled water. After drying under vacuum, the esters (25.0 g.) were distilled at 4 mm pressure to the following fractions (Table II).

TABLE II

Fraction.	B. P.	Net wt.	Sap. equiv.	I. V.	Methyl laurate.
S_1	115-120°	1.1865 g.	213.0	1.2	1.1865 g
S_2	120-125°	11.9774	214.0	1 2	11 9774
S_3	125-130°	8 4920	215.1	1.3	8.4920
S_4	130-135°	2.1490	216.0	1.3	2.1490
Residue	...	1.0240	...	...	1.0240
Loss	...	0.1711	...	...	...
Total	...	25.000	...	...	24.8269

All these fractions were saponified separately and the corresponding acids were liberated and these were fractionally crystallised from dilute alcohol and acetone.

Acids from fraction S_1 had the mean M.W. of 200.1 and m.p. 43-44°. These were identified as lauric acid by its mixed melting point with an authentic sample of lauric acid.

Acids from fraction S_2 had the mean M.W of 201.4 and m. p. 43°. These were identified as lauric acid by its mixed melting point with an authentic sample of lauric acid.

Similarly, the acids obtained from the fractions S_3 and S_4 were identified as lauric acid and the mother-liquors from the above crystallisation of the acids left on evaporation a very little residue which did not show the presence of any other acids.

Liquid Acids.—Methyl esters of the liquid acids were prepared in the usual manner and 37.0 g. of these was fractionated at 4 mm pressure to the following fractions (Table III).

TABLE III

Fraction.	B. P.	Net wt.	I. V.	Sap. equiv.	Component methyl esters.		
					Caprate.	Laurate.	Oleate.
L_1	100-110°	1.5606 g.	1.0	190.0	1.306 g.	0.2546 g.	...
L_2	110-120°	4.1755	1.1	199.0	2.030	2.1455	...
L_3	120-130°	8.7575	1.1	201 0	3.731	5.0265	...
L_4	130-140°	12 1450	1.1	214.0	...	12.1450	...
L_5	140-150°	6.5750	22.3	230 0	...	4.9250	1.650 g.
L_6	150-160°	3.2790	42.1	240.0	...	1.9790	1.300
Residue	...	3.3210	...	...	...	0.1710	0.150
Loss	...	0 1864	...	...	...	...	...
Total	...	37 00...	...	...	7.067	26.5466	3 100

The above fractions were saponified and the corresponding acids were examined separately.

Acids from fraction L_1 had the mean M. W. 176.0 and were liquid. This showed the presence of some acid with a molecular weight lower than that of lauric acid, possibly teh capric acid.

Acids from L_2 had the mean M.W. 185.4, thus showing the presence of some lower molecular weight acid. This was separated by the fractional distillation of the mixed acids from the above mentioned fraction. The fraction of the acids which distilled at 266-69° was collected separately and this was refractionated to get a pure sample of the acid (b. p. 268-269°). There was no other fraction which distilled below this temperature, thus showing the absence of *n*-octanoic and hexanoic acids. The molecular weight of the acid of b.p. 268-69° was found to be 171.4 by silver salt method (Clarke, "A Handbook of Organic Analysis", 1949, 4th Ed., p. 315) and identified as capric acid (M.W. calc. 172.0).

The residual acid (m. p. 43-44°) was identified as lauric acid by crystallisation from dilute alcohol and dilute acetone and finding out its mixed melting point with an authentic sample of lauric acid which remained unchanged.

Similarly capric acid was also separated from fraction L_2 by the above mentioned method and confirmed by its mean M.W. 171.3 by the silver salt method. The solid acid in the residue was identified as lauric acid by crystallisation from dilute alcohol and dilute acetone and by mixed m. p. with an authentic sample of lauric acid, m.p. 43-44°.

Acids from the fractions L_4, L_5 and L_6 had the mean M.W. 200.1, 216.0 and 226.1 respectively. These were crystallised from dilute alcohol and dilute acetone and the solid acid melting at 43-44° was found to be lauric acid which was identified by its mixed m. p. with an authentic sample.

Evaporation of the solvent from the mother-liquors from the fractions L_4, L_5 and L_6 yielded a liquid residue in each case and showed the iodine absorption which indicated the presence of an unsaturated acid. The unsaturated acid was oleic acid which was confirmed by carrying out the oxidation of the potassium salt of residual acids from the fractions L_4, L_5 and L_6 in cold alkaline solution with dilute potassium permanganate

by Lapworth and Mottram's method (*J. Chem. Soc.*, 1925, 1628). From the resultant acids dihydroxystearic acid, m. p. 130-131°, mean M. W. 318.0, was isolated. This confirmed the presence of oleic acid.

The above data calculated as per example recorded in Part I (this *issue*, p. 139) gave the following components in the mixed fatty acids: lauric acid, 83.89%; capric acid, 10.08%; oleic acid, 4.56% and unsaponifiable matter, 1.47%.

Unsaponifiable Matter.—The unsaponifiable matter was found to be mainly consisting of waxes, hydrocarbons, higher alcohol and a very minute quantity of sterol, but the amount of it was too small for further examination.

Sincere thanks of the authors are due to Dr. Sadgopal, Senior Research Officer-in charge, Chemistry of Forest Products Branch, Forest Research Institute, Dehra Dun, for the keen interest he has taken during the investigation and also to the President, F.R.I. and Colleges, Dehra Dun, for allowing the facilities to one of the authors (S.A.N.) for this work to be carried out in this Institute.

CHEMISTRY OF FOREST PRODUCTS BRANCH,
FOREST RESEARCH INSTITUTE,
DEHRA DUN.

Received February 1, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 2, 1957]

STUDIES ON THE POTENTIOMETRIC DETERMINATION OF ASCORBIC ACID IN FRUIT AND VEGETABLE EXTRACTS

By G. Sitaramaiah

A satisfactory potentiometric procedure for the determination of the ascorbic acid content of fruit and vegetable extracts, using a Hg-Pt electrode, has been described

The titrimetric determination of ascorbic acid with 2 : 6-dichlorophenol indophenol, originally suggested by Tillmans (*Untersuch. Lebensm.*, 1927, **54**, 33) and later modified by Bessey and King (*J. Biol. Chem.*, 1933, **103**, 687), is the most widely used method to-day. This method has been adapted to the photometric determination of ascorbic acid, a method not quite suited for highly pigmented and turbid extracts. To meet such difficulties a potentiometric method with special Hg—Pt double electrode was suggested (Harris *et al.*, *Biochem. J.*, 1942, **36**, 183) but the electrode tended to become sluggish in concentrated extracts. The present investigation was undertaken with a view to evolving a satisfactory potentiometric procedure for the determination of ascorbic acid content of fruit and vegetable extracts.

Experimental

A saturated calomel electrode with a KCl-agar salt bridge was used as a reference electrode and the titrations were carried out in CO_2-atmosphere. Potential measurements were made with a Vernier potentiometer.

Gold-coated, mercury-coated and silver-coated platinum electrodes as well as bright and platinised platinum electrodes were used so as to select the most suitable electrode among these for the accurate estimation of ascorbic acid.

All solutions were prepared as prescribed in "Methods of Vitamins Assay" (1951). The fruit and vegetable extracts were prepared as described by Bessey and King (*loc. cit.*).

The platinum electrode, in general, was found to take a long time to attain equilibrium, and a continuous drift of potential was noticed during the titration. The silver-coated platinum electrode was found unsuitable in these titrations, since no point of inflexion was observable in the curves (Fig. 1).

A rod-type platinum electrode, coated with a thin layer of mercury, was observed to respond well to each addition of the dye in ascorbic acid solutions, stabilised with oxalic or metaphosphoric acid.

The influence of the time of electroplating on the maximum increase of potential at the end-point for the addition of 0.05 c. c. of the dye (0.025%) was first studied. The results are summarised in Table I.

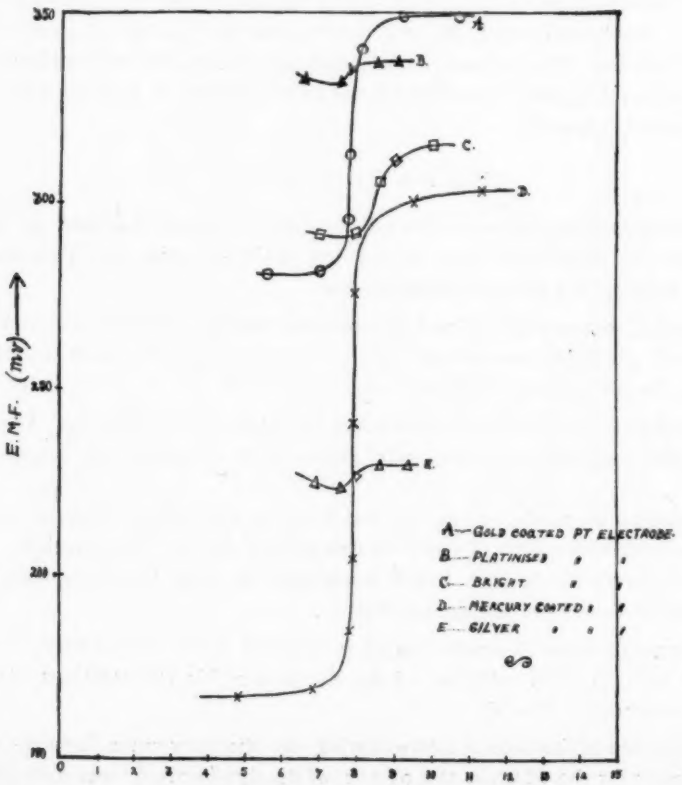
TABLE I

Behaviour of the Hg-*coated* Pt *electrode under diff. conditions.*
Time for attaining equilibrium : ~1min.

No.	Time of electroplating the electrode.	* Max. increase in potential.	End-point. Visual.	End-point. From the curve.	% Diff.
1	30 sec.	28 mv	8.0 c.c.	7.95 c c.	0 6
2	,, (with KCl)	36	8 0	8.00	0.0
3	45	29	8.0	7.95	0.6
4	,, (Do)	38	8.0	8.00	0.0
5	2 mins.	15	8 0	7.95	0.6
6	,, (Do)	18	8 0	7.95	0.6
7	10	13	8 0	7.95	0.6
8	,, (Do)	16	8.0	7.95	0.6
9	30	15	8.0	7 90	1.25
10	,, (Do)	15	8.0	7.90	1.25

* For 0.05 c.c. of the dye.

FIG. 1



As seen from Table I, a better response is observable with a very thin coating of mercury on the electrode ; an electrode, coated with mercury for 45 seconds, gives the maximum increase in potential (29 mv) and this increase is enhanced to 38 mv when a small amount (0.1 c.c.) of saturated potassium chloride is present. Further, the addition of potassium chloride has a stabilising effect on the E.M.F. These observations support the theory of Harris *et al. (loc. cit.)* that the Hg-Pt electrode behaves as a mercury electrode, but when an excess of the dye is present, the metallic mercury changes to Hg^{2+} ions and the electrode behaves as a platinum electrode.

A platinum electrode with a thick coating of gold responded satisfactorily in these titrations. The inflexion at the end-point for the addition of 0.05 c.c. (0.025%) of the dye solution was found to be 20 mv.

The stabilising medium, either oxalic or metaphosphoric acid, was not found to have any significant influence on the nature of the curves obtained with the different electrodes.

The dye solution (0.025%) after standardisation by titration with standard ascorbic acid (1 mg. in 10 c.c. of 3% metaphosphoric acid) can satisfactorily be used for the determination of the ascorbic acid content of fruit and vegetable extracts.

TABLE II

Comparison of values of ascorbic acid obtained with Hg-Pt *and gold-plated platinum electrodes.*

No.	Name of fruit of vegetable.	Hg—Pt electrode. End-point from the curve.	Hg—Pt electrode. Ascorbic acid (mg./100 g.).	Gold electrode. End-point from the curve.	Gold electrode. Ascorbic acid (mg./100 g.).
1	Orange juce	6.60 c.c.	24.0*	6.55 c.c.	23.8*
2	Tomato	7.90	28.7	7.85	28.6
3	Onion	3.85	14.0	3.85	14.0
4	Mint leaves	22.85	83.1	22.65	82.4
5	Spinach leaves	12.65	46.0	12.55	45.6

* The ascorbic acid content is given in mg /100 c.c. of the juice.

From the results Hg—Pt double electrode appears to be a satisfactory electrode for the determination of ascorbic acid ; however, a gold electrode can also be used as an alternate electrode where a check on the Hg—Pt electrode becomes necessary.

The author records his appreciation of the interest taken by Dr. R. D. Gupta, M.Sc., Ph.D., A.R.I.C., Head of the Chemistry Department.

CHEMICAL LABORATORIES,
BIRLA COLLEGE OF SCIENCE,
PILANI (RAJASTHAN).

Received May 10, 1956.

SHORT NOTES

ATOMIC AND STRUCTURAL RHEOCHORS

By R. P. Shukla

Rheochor can be as useful as parachor in predicting the structures of organic compounds. It can also be used for finding the viscosities of liquids (Shukla and Bhatnagar, *J. Phys. Chem.*, 1955, **59**, 988). But because of the lack of consolidated data on the atomic and structural rheochors, it has not been possible to use it. Bhagwat, Toshniwal and Moghe (this *Journal*, 1944, **21**, 30) have used the equation $M\eta^{\frac{1}{4}}/d$ for finding the rheochor of substances, while Subnis, Bhagwat and Silawat (*ibid.*, 1946, **26**, 534) have used the equation $M(\eta \times 10^3)^{\frac{1}{4}}/d$, and hence, according to Bhagwat *et al.* (*loc.cit.*) the value for methyl alcohol is 21.33, while Subnis *et al.* (*loc. cit.*) have suggested the value 50.3. The present work has been undertaken to co-ordinate the results of the two workers and to have consolidated data on rheochor. The results obtained in the present investigation are recorded in Table I.

Table I

[M,d, and R have usual the significance. All the viscosities are in centipoises and we have used the formula suggested by Newton Friend, *Nature*, 1942, **148**, 432].

No.	Substance	'M'.	'd'.	$\eta \times 100$	'R'.
1.	Ethyl ether	74 12	0.7146	0.25	49 00
2.	*iso*Propyl ether	102 17	0.7244	0.34	69 33
3	Butyl ether	130.22	0.7694	0.69	90 84
4.	Acetone	56.08	0.7910	0.35	36 21
5.	Methyl *iso*butyl ketone	100.16	0 8042	0.59	65.46
6.	Methyl amyl ketone	114.18	0.8166	0.65	74.35
7.	Benzene	78.00	0.8646	0 57	47 29
8.	Butylamine	73 14	0.7385	0.50	80 95
9.	Mercaptoethanol	78.13	1.1198	3.43	45.76
10.	Trichloroethane	133 42	1 4432	1 20	53.19

All the values are at 20°.

The difference for CH_2 has been calculated from sets of values shown below.

Table II

S. No.	System	Value for CH_2.
2–1	*iso*Propyl ether—ethyl ether	2(10 14)
3–1	Butyl ether—ethyl ether	4(10 45)
3–2	Butyl ether—*iso*propyl ether	2(10.75)
6–5	Methyl *iso*butyl ketone—acetone	3(9.75)
7–5	Methyl amyl ketone—acetone	4 (9 53)
7–6	Methyl amyl ketone—methyl*iso*butyl ketone	(8 86)
		Average 9 91

In the present work all the non-associated liquids have been taken and the value determined. As will be seen, it comes to be 9.91. Substituting this value in *n*-hexane one obtains the value for H atom as 2.06 and C as 5.89.

While from ether the value for O comes to be 5.34. Similary by substituting the values in different compounds, the following results have been obtained.

TABLE III

S. No.	1	2	3	4	5	6	7	8
Atom	H	C	O	Cl	S	N	Double bond	Six—membered ring
Value	2.01	5.98	5.34	11 79	23.84	35.28	1.14	−3.73

The author wishes to thank Messrs. Carbide and Carbon Chemicals Corporation, U.S.A. for supplying the data.

DEPARTMENT OF CHEMISTRY,
HOLKAR COLLEGE, INDORE.

Received April 23, 1956.

DETECTION OF COBALT BY *o*-PHENYLENEDIAMINE

BY R. L. DUTTA

o-Phenylenediamine has earlier been proposed as a reagent for the detection of nickel and vanadium. Nickel yields in presence of ammonia a bluish purple precipitate (Welcher, "Organic Analytical Reagents", Vol. II, p. 430 ; Feigl, *Oestr. Chem. Ztg.*, 1923, **26**, 85; 1927, **30**, 13 ; *Monatsh.*, 1927, **48**, 445). But the test does not respond in dilute solutions, as the complex under these conditions is wholly dissociated into its constituents (Heiber *et al.*, *Z. anorg. allgem. Chem.*, 1929, **180**, 89). *o*-Phenylenediamine hydrochloride develops an orange-yellow colour with a vanadate (Rosenthaler, *Mikrochem.*, 1937, **23**, 194), but the test is not a sensitive one for vanadium. It has been observed that interaction of *o*-phenylenediamine with cobalt and dimethylglyoxime produces an intense unstable colour (Lee and Diehl, *Proc. Iowa Acad. Sci.*. 1950, **57**, 187 ; *Chem. Abs.*, 1951, 7911) but no study of the interaction of cobalt and *o*-phenylenediamine, with particular reference to its applicability as a means of detecting cobalt, has been made. It has now been observed that *o*-phenylenediamine alone gives rise to an intense violet coloration with traces of cobalt in alkaline medium.

Qualitative detection of cobalt was carried out in aqueous medium. In aqueous medium the development of the violet colour is not immediate but requires a little time and shaking. Calcium, strontium, barium, magnesium, zinc, cadmium, lead, beryllium, aluminium, thallium, uranium, thorium, zirconium, titanium and bismuth do not interfere. Manganese intereferes due to precipitation of higher manganese oxides in the alkaline medium. Ferric iron, silver, mercuric mercury etc. immediately oxidise the

reagent to an intense red colour, the metallic ions being reduced respectively to ferrous iron, metallic silver and mercury. Palladium develops a greenish blue precipitate or colour with violet fluorescence. Copper develops a violet unstable colour. But many of these interfering ions can be advantageously masked for the test. Of the anions, iodide, bromide, chloride, sulphate, acetate, nitrate, nitrite, borate, tungstate, vanadate, oxalate, phosphate, molybdate, fluoride, bromate and iodate do not interfere. Oxidising anions such as persulphate, dichromate, chromate, ferricyanide should not be present in more than trace quantities, as they oxidise the reagent immediately. Ions such as sulphite, ferrocyanide, when present even in small quantities, develop precipitates or colours with cobalt, and hence, should be absent. Thiosulphate or thiocyanate does not interfere when present in quantities usually encountered in qualitative detection. Citrate, tartrate, cyanide and ethylenediamine tetra-acetate mask cobalt and so they should be absent.

The exact nature of the coloured product, however, could not be established. The violet colour was extracted with *iso*amyl alcohol and the extract evaporated to dryness. The residue left showed positive test for cobalt. An aqueous hexammine cobaltic chloride solution, when treated with *o*-phenylenediamine solution and a trace of alkali and slightly warmed, immediately gives the violet colour. These qualitative tests indicate that the coloured product is an unstable cobaltic derivative.

A 0.2% aqueous solution (freshly prepared) of the reagent was used. Ammonia and sodium hydroxide may be used with equal advantage to make the medium alkaline; pyridine serves the purpose less readily. The violet colour is extractable with *iso*amyl alcohol. The visual sensitivity was found to be 0.1 γ Co in a concentration limit $1 : 10^7$ parts. The colour reaction appears to be more sensitive than rubeanic acid (Rây, *Z. anal. Chem.*, 1929, **79**, 94).

The reagent solution did not keep well and was always freshly prepared. The reaction being highly sensitive, it was found advantageous to work with 1 c.c. of a dilute solution containing 0.2 mg. of Co per c.c. and to compare the colour against blanks. The procedures for detection of cobalt in presence of different metallic ions are described below.

The reagent solution (1 c.c.) was added to the solution containing Co with Zn, Al, Be, Cd and Pb, followed by sufficient NH_4OH or NaOH to dissolve the precipitates of the hydroxides. A violet colour then developed on shaking.

When Ti, U, Th, and Zr were present, the violet colour appeared in the supernatant solution. Coloured product should be extracted with *iso*amyl alcohol in presence of enough NaOH when Cr is present. The effect of Fe^{III} could be masked by the addition of NaF to the solution, rendered just ammoniacal and the coloured product might be extracted with *iso*amyl alcohol. Similarly, the effect of Ag and Pd could be inhibited by the addition of pyridine (1-2 c.c.) and of Hg by excess KI before the addition of the reagent and ammonia.

In presence of Ni, 1 c.c. of the reagent was added followed by 2 c.c. of 1 : 2 NH_4OH to get a clear solution and after a few minutes' shaking, the colour was extracted with

*iso*amyl alcohol. The blank alcoholic layer (with nickel -*o*-phenylenediamine) is either colorless or pale bluish. The test must be carried out in the cold and an excess of the reagent should be avoided.

An exhaustive spectrophotometric study of the colour reaction was made. But the colour was found to be unstable and highly sensitive to p_H changes. The coloured product has two absorption maxima: 550mμ and 750mμ.

Author's grateful thanks are due to Prof. P. Rây and to Dr. P. C. Banerjee for their kind interest as also for extending laboratory facilities. Financial assistance by the Ministry of Education, Government of India, is gratefully acknowledged.

Inorganic Chemistry Laboratory,
Indian Association for the Cultivation of Science,
Calcutta-32.

Received September 4, 1956.

Published March 1956

A book that should find place on the shelves of every Library

HISTORY OF CHEMISTRY IN ANCIENT & MEDIEVAL INDIA

Incorporating

HISTORY OF HINDU CHEMISTRY

by Acharya Prafulla Chandra Ray

Edited by PROF. P. Rây

Royal 8*vo*. Rexin bound, 494 pages with illustrations.

Price *ex*-postage: Prime Edition:—Rs. 24/- Ordinary Edition—Rs. 20/-
For Fellows ,, ,, Rs. 20/- ,, ,, Rs. 16/-

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY

The book is invaluable to students of science and history and to all persons interested in the heritage of India.

Nature, January 5, 1957.

"Since there is much new material in the book, all those who are fortunate enough to have the earlier edition will wish to have the new one. ... ...

All those interested in the History of Chemistry owe a debt of gratitude to Prof. P. Rây and the Indian Chemical Society for its publication".

J. R. Partington.

Inland Rates of Advertisement

In Ordinary Pages:
(Single insertion)

Full Page	...	... Rs. 40/-
Half Page	...	... ,, 25/-
Quarter Page	...	... ,, 15/-

In Cover Pages:

Cover (Back) Full	...	Rs. 100/-
,, ,, Half	...	,, 60/-

Second and Third Pages:

Full Page	...	Rs. 70/-
Half Page	...	,, 40/-
Quarter Page	...	,, 25/-

In special positions:

Page facing first reading matter	...	Rs. 70/-
Page facing last page of reading matter	...	,, 60/-
Page facing inside front cover	...	,, 50/-
Page facing inside back cover	...	,, 50/-

Closing date for advertising materials: 7th of the previous month.

The above rates apply also to the *Indian Journal of applied Chemistry.*

10% *Rebate allowed in cases of six consecutive full and half page insertions.*

All communications are to be addressed to:

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY
92, Upper Circular Road, Calcutta-9.

For Laboratory *Reagent Quality* Acids

To Precise Specifications

Maximum Limits of Impurities:	Acid Sulphuric H_2SO_4: 98% w/w Sp. gr. 1.840 at 15°.	Acid Nitric HNO_3: 69.8% w/w Sp.gr. 1.420 at 15°.	Acid Hydrochloric HCl: 35.39% w/w Sp. gr. 1.8 at 15°.
Non-Volatile Matter :	0.0025 %	0.001 %	0.0015 %
Chloride (Cl) :	0.0003 %	0.0001 %	—
Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

We invite orders and enquiries.
Write us about your requirements for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ld.

CALCUTTA :: BOMBAY :: KANPUR

Office : 6, Ganesh Chunder Avenue, Calcutta-13

All In One

INDEX

REAGENT BOTTLES

made by

Sigcol

Sole Distributors

GHARPURE & CO.

P36, ROYAL EXCHANGE PLACE

EXTENSION • CALCUTTA-1

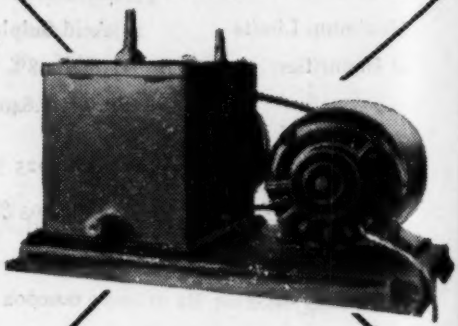
GRAM: MEENAMO PHONE: 22 2061

MADE IN INDIA

HIGH VACUUM ROTARY PUMP

Single Stage & Two Stage

Suitable for Laboratory use and similar in performance to those made in Germany, England & U. S. A.



All Indian Materials and Constructions.

BASIC & SYNTHETIC CHEMICALS PRIVATE LTD

P. O. Jadavpur College, Calcutta-32

GS Gas PLANTS

FOR

HEATING

IN

LABORATORY

INDUSTRY

KITCHEN

GANSONS

PRIVATE LIMITED.

P.O.B. 5576. BOMBAY-14.

—Also makers of—

Superior Laboratory Fittings

Atomic Equipments.

* OIL GAS PLANTS

* WOODEN FURNITURE

for Homes, Offices &

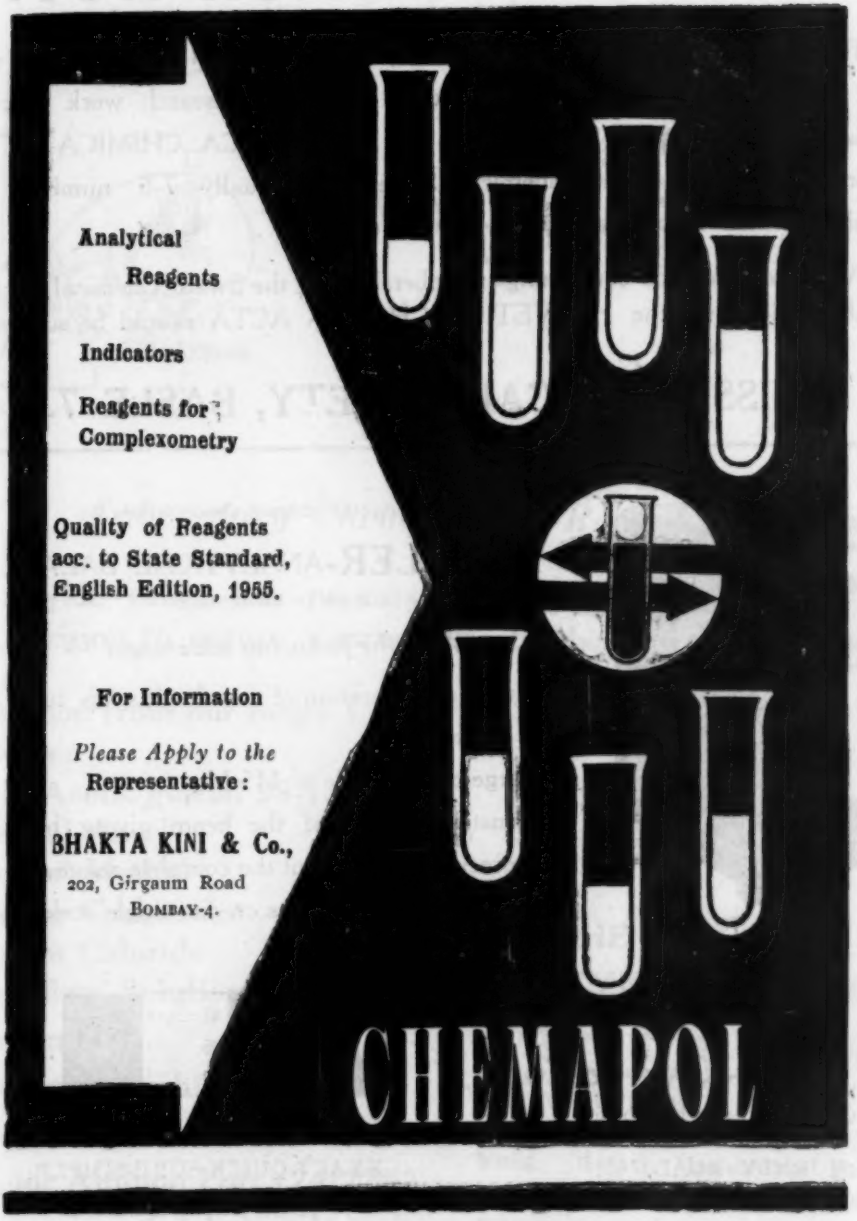
LABORATORIES

* SCIENTIFIC APPARATUS & INSTRUMENTS

MANSFIELD OIL GAS CO., LTD.,

16, Radhanath Chowdhury Road, Calcutta-15.

301, Linghi Chetty Street, Madras-1.



PRAHA, CZECHOSLOVAKIA

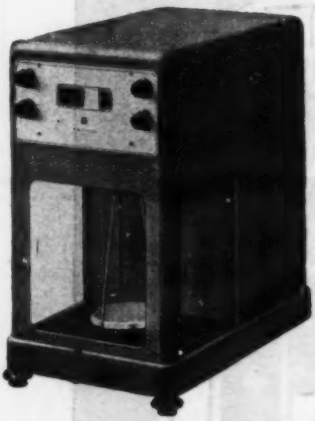
V

HELVETICA CHIMICA ACTA

The HELVETICA CHIMICA ACTA, founded in 1918, publishes in one of the three national languages the principal results of research work in pure chemistry carried out in Switzerland. The HELVETICA CHIMICA ACTA are property of the Swiss Chemical Society. Annually 7-8 numbers are published which members receive without charge.

All correspondence concerning membership of the Swiss Chemical Society or subscriptions for the HELVETICA CHIMICA ACTA should be addressed to :

SWISS CHEMICAL SOCIETY, BASLE 7.



The competent chemist always prefers the

METTLER-ANALYTICAL BALANCE

MADE IN SWITZERLAND

With the following advantages :—

-Automatic operation of the weights up to 200 Grams.

-Large optical scale of 115 Mgs.

-Constant loading of the beam giving highest precision throughout the complete range.

-Reading of the weights on one single scale.

Sole Agents :—

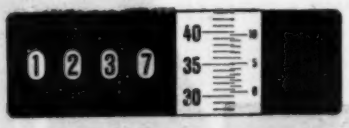
RAJ-DER-KAR & Co.

COMMISSARIAT BUILDING

HORNBY ROAD,

FORT BOMBAY.

Telephone. 27304. Telegram : 'Techlab'

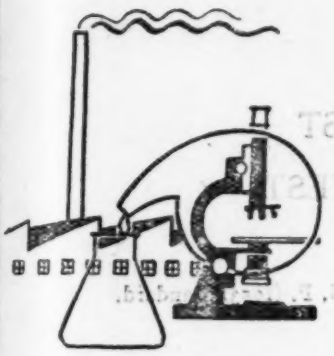


Weight = 123.7306 grams.

-EXACT-QUICK-SURE-SIMPLE.

-Service facilities available at BOMBAY, MADRAS & CALCUTTA.

Ask for offers and detail literature.



SERVING for LAST 40 YEARS

Laboratory Chemicals & Reagents

of a wide range are manufactured by us under expert supervision to ensure guaranteed standard & reliability.

A selection from our range :

- Acetone
- Acid Acetic glacial 99-100%
- Alcohol Amyl
- Alcohol Methyl
- Barium Carbonate
- Barium Chloride
- Benedicts' Solution
- Benzene
- Carbon Tetrachloride
- Lead Acetate
- Liquor Ammon Fort (24/27%)
- Magnesium Sulphate XL

THE CALCUTTA CHEMICAL CO., LTD.

HEAD OFFICE: 35, Panditia Road, Calcutta 29.

BRANCH OFFICES & DEPOTS AT : Delhi, Madras, Bombay, Bangalore, Vizag., Nagpur, Jamshedpur, Patna, Ranchi, Bhagalpur, Madhupur, Asansol, Siliguri.

SPECIALLY MADE

Apparatuses

For

* BOILING POINT TEST
* FREEZING POINT TEST.
* ARSENIC TEST.

B. P. (1953) Standard.

Please Enquire to

SCIENTIFIC GLASS APPARATUS MFG. CO.

11/2 Harinath Dey Road, Calcutta-9

Phone : East 4411. Gram : Sigamko,

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

THE EMIL GREINER CO.

NEW YORK, U.S.A.

World's leading manufacturers of Petroleum Testing Equipment for 75 years.

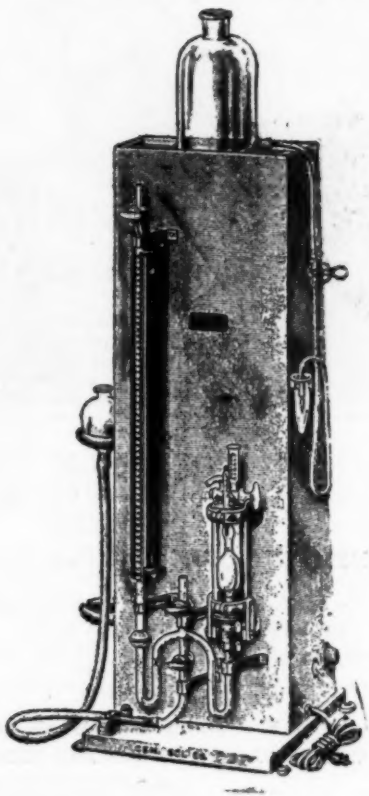
*

SOLE REPRESENTATIVES IN INDIA

LABORATORY FURNISHERS

DHUN MANSION
VINCENT ROAD, DADAR.
BOMBAY 14.
Branch : AHMEDABAD.

CENCO IMPROVED DESIGN

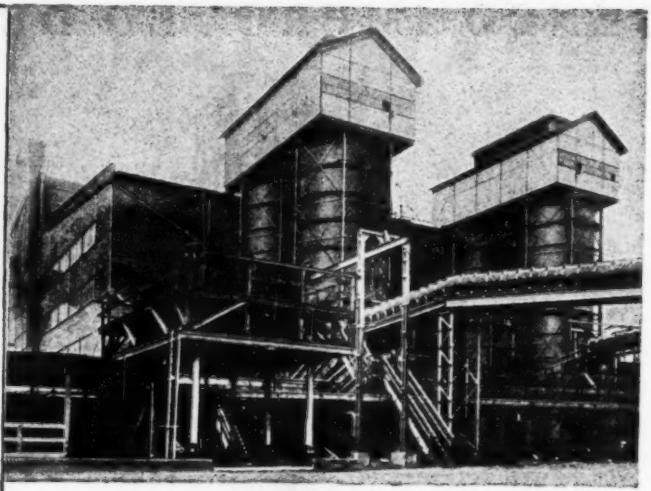


Van Slyke Manometric Blood Gas Apparatus for the determination of oxygen, carbon monoxide and nitrogen in whole blood or blood plasma as well as carbon-dioxide absorbing power. May also be used for micro determinations of organic nitrogen and carbon, urea, amino-nitrogen, iodates, sulphates, sugar, calcium, lactic acid, total base, nitrates and potassium; and analyses of gas mixtures. More accurate than apparatus employing volumetric method. The improvement incorporated by Cenco in their design over that used by Dr. Van Slyke and his associates does not involve any change in principles and measurement techniques but by rigid construction and finer mechanical and lighting features increases the ease and accuracy of measurement.

SOLE DISTRIBUTORS:

THE SCIENTIFIC INSTRUMENT Co. Ltd.

ALLAHABAD, BOMBAY, CALCUTTA, MADRAS, NEW DELHI.



WE DESIGN
DELIVER &
ERECT

COMPLETE EQUIPMENT FOR H_2SO_4 PRODUCTION

WE SHALL OFFER TO YOU TECHNICAL UNITS
OF THE FOLLOWING OUTPUTS:

Raw material: SULPHUR		PYRITE	
10 mt/24 hrs.		50 mt/24 hours	
25 mt/24	,,	100 mt/24	,,
50 mt/24	,,	150 mt/24	,,

WE SHALL GUARANTEE A SUITABLE
AND UP-TO-DATE DESIGN AND ECONOMIC OPERATION

TECHNOEXPORT

Praha—Czechoslovakia

For informations please contact

TRADE REPRESENTATION OF CZECHOSLOVAK REPUBLIK,

BOMBAY BRANCH: KASTURI BUILDING, JAMSHEDJI TATA ROAD, BOMBAY.

CALCUTTA BRANCH: P-38, MISSION ROW EXTN., CALCUTTA.

X

Please visit Czechoslovakia Exhibition in Colombo from March 9—31st 1957.

FOR RAPID & ACCURATE CHEMICAL ANALYSIS

USE

TINSLEY

POLAROGRAPH (with derivative circuit)

Here are some advantages:

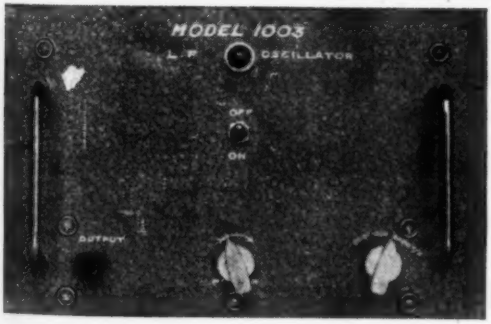
* MICRO ANALYSIS
* HIGH SENSITIVITY
* QUALITATIVE AND QUANTITATIVE ESTIMATION
* SIMULTANEOUS ESTIMATION OF SEVERAL CONSTITUENTS ON ONE POLAROGRAM
* ADAPTABILITY: ANALYSIS OF METALS, ORGANIC & INORGANIC SUBSTANCES ON THE SAME SAMPLE
* REPEATED ANALYSIS
* SIMPLIFIED OPERATION FOR USE BY SEMI-SKILLED STAFF
* ROUTINE ANALYSIS WITH SPEED AND ACCURACY.

For further particulars, please contact Sole Agents in India

PIONEER INDUSTRIES

1, Mango Lane, CALCUTTA-1. | 139, Medows Street, (Ground Floor) BOMBAY-1. | 193, Mount Road MADRAS-2.

ELECTRONIC INSTRUMENTS FOR CHEMICAL LABORATORIES



1003 is a twin-T type oscillator for Bridge measurement. Excellent wave form, distortion less than 3%, adequate power, adjustable up to 2.5 watts. max. Oscillator frequency 500, 1000 and 2000 cps.

Also Available:

Apparatus for measurement of dielectric polarisation using heterodyne beat principle.

EMISSION RADIO & VARIETIES.

120, LOWER CIRCULAR ROAD, CALCUTTA-14.

Phone—24-2513

Phone—34-3176. Telegrams—Nadiachemi.

NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA

Manufacturers of :—

1. *CHEMICALS*—**Benzene, Toluene, &c., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals.**
2. **STILLS for distilling Essential Oils, Alcohols, Water, etc.**

   RECTIFIERS, CONDENSERS, &c.
3. **OVENS, Baths &c for Gas, Oil or Electric heatings.**
4. **Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, &c.) of both Glass and Metal.**
5. **MICRO-ANALYSIS APPARATUS.**

Please ask for Estimates.

PRESIDENT :

P. K. Bose, D.Sc., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

N. R. Dhar, D.Sc., Dr.es.Sc., F.R.I.C., F.N.I.
B. B. Dey, D.Sc., F.R.I.C., F.N.I.
Sir J. C. Ghosh, Kt., D.Sc., F.N.I.
B. C. Guha, D.Sc., Ph.D., F.N.I.
P. C. Guha, D.Sc., F.N.I.
J. N. Mukherjee, C.B.E., D.Sc., F.A.S.B., F.N.I.
Mata Prasad, D.Sc., F.R.I.C., F.N.I.
J. N. Ray, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. Ray, M.A., F.N.I.
B. K. Singh, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

U. P. Basu, D.Sc., F.N.I.
B. Sanjiva Rao, D.Sc., Ph.D., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.R.I.C., F.N.I.
R. D. Desai, D.Sc., F.R.I.C., F.N.I.
President of Ahmedbad Branch (*ex-officio*).

HONY. SECRETARY :

S. K. Mukherjee, D.Sc.

HONY. TREASURER :

B. N. Ghosh, D.Sc., F.N.I.

MEMBERS OF THE COUNCIL :

N. Adhikari, M.Sc.
D. K. Banerjee, D.Sc.
D. Chakravarti, D.Sc., F.N.I.
Mrs. Ashima Chatterjee, D.Sc.
B. Chatterjee, D.Sc.
A. C. Chatterji, D.Sc., Dr. Ing., F.N.I.
H. N. Das Gupta, D.Sc.
S. S. Joshi, D.Sc., F.R.I.C., F.N.I.
T. N. Ghosh, D.Sc., F.N.I.
J. Gupta, D.Sc.
A. N. Kappanna, D.Sc., F.N.I.
R. P. Mitra, D.Sc. F.N.I.
S. M. Mukherji, D.Sc., Ph.D.
P. V. Nair, M.Sc., D.Phil.
A. B. Sen M.Sc., Ph.D.
V. Subrahmanyan, D.Sc., F.R.I.C., F.N.I.
L. M. Yeddanapalli, M.A., Ph.D., D.Sc., F.R.I.C.
S. H. Zaheer, M.A., Ph.D.

HONY. EDITORS :

S. R. Palit, D.Sc., F.R.I.C., F.N.I.
R. C. Shah, D.Sc., F.N.I.

BOARD OF ASSOCIATE EDITORS :

D. K. Banerjee, D.Sc.
P. K. Bose, D.Sc., F.N.I.
B. Chatterjee, D.Sc.
J. K. Chowdhury, M.Sc., Ph.D., F.N.I.
P. C. Dutta, D.Sc.
B. N. Ghosh, D.Sc., F.N.I.
J. C. Ghosh, D.Sc., F.N.I.
A. N. Kappanna, D.Sc., F.N.I.
S. K. Mukherjee, D.Sc.
B. C. Guha, D.Sc., Ph.D., F.N.I.
P. Ray M.A., F.N.I.
T. R. Seshadri, M.A., Ph.D., F.N.I.
P. B. Sarkar, Dr.es. Sc., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.N.I.

HONY. AUDITORS :

P. C. Nandi, M.A., B.Sc., A.C.A.R.A.
A. B. Gupta, B.Sc., L.L.B., A.C.A.R.A.

Asst. Secretary:
B. C. Roy, M.Sc.

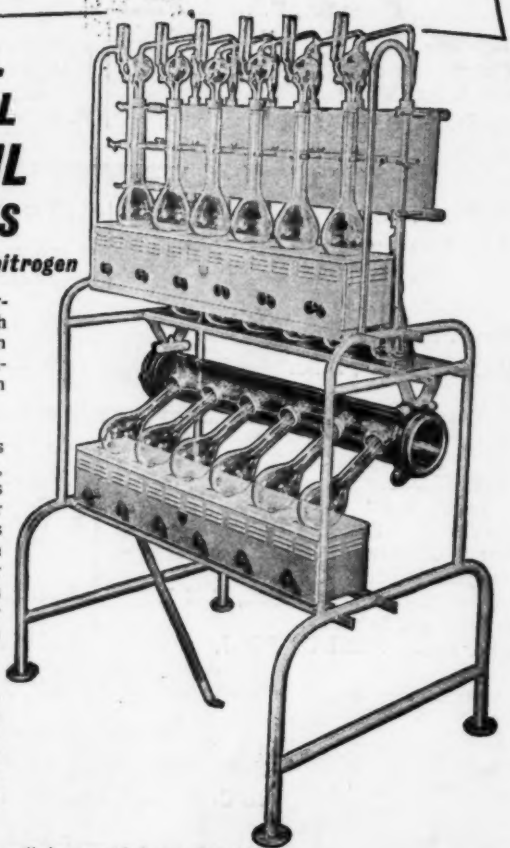
Asst. Editor :
G. Banerjee, M.Sc.

Regtd. No. C1878

B.T.L. INSTRUMENT INFORMATION

THE B.T.L. UNIVERSAL KJELDAHL APPARATUS

for the determination of nitrogen



- comprises a range of interchangeable components which can be readily assembled in the form of digestion, distillation or combined digestion and distillation units.
- The range of components cover gas or electric heating, various types of condensers and splash heads, and water manifolds. The components are supplied for assembly in units of six tests. For larger installations two or more units may be coupled together for any desired number of tests in multiples of six.
- The illustration shows an example of the use of the range of components in producing a typical Kjeldahl assembly. An extension frame is fitted at one end so that further six test assemblies can be added.

Full details will be provided on request

BTL **BAIRD & TATLOCK (LONDON) LTD.**

SOLE AGENTS IN INDIA :

TOSHNIWAL BROTHERS (PRIVATE) LTD.

198, Jamshedji Tata Road, FORT, BOMBAY-1.

Branches :

9, Blackers Road, MADRAS-2.

14-B/4 N.E.A. Uttari Marg NEW DELHI-5.

Also at Calcutta

Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunge, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.